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DEPARTMENT OF PHYSICS
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OLD DOMINION UNIVERSITY
NORFOLK, VIRGINIA

Technical Report PTR-81-6

HIGH-RESOLUTION LASER ADSORPTION SPECTROSCOPY OF OZONE NEAR 1129.4 cm^{-1}

By

Lawrence N. Majorana

Principal Investigator: Gary E. Copeland

Final Report

For the period October 25, 1979 - October 24, 1981

Prepared for the
National Aeronautics and Space Administration
Langley Research Center
Hampton, Virginia

Under

Research Grant NAG1-1
James M. Hoell, Technical Monitor
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ABSTRACT

HIGH-RESOLUTION LASER ABSORPTION SPECTROSCOPY OF OZONE NEAR 1129.4 CM-1

Lawrence N. Majorana
Old Dominion University, 1980
Director: Dr. Gary Copeland

A Beer's Law experiment was performed with a tunable diode laser to determine self broadened line shape parameters of one infrared absorption ozone line in the ν_1 band for ten pressures from 0.26 to 6.29 Torr at 285K. SO_2 line positions were used for wavelength calibration. Line shapes were iteratively fitted to the Voigt function at a Doppler width of 29.54 MHz (HWHM) resulting in values for the integrated line strength, (S) , of $(0.144 \pm 0.007) \times 10^{-20}$ cm-1/molecule cm-2, line center frequency, (ν_0) , of 1129.426 cm-1 and the Lorentzian contributions to halfwidth, (α_L) . A linear least squares fit of α_L as a function of pressure yielded a zero intercept of 15.27 ± 0.29 MHz ($\rho = 0.99$) and a broadening parameter, (α_0) , of 5.71 ± 0.29 MHz/Torr. This results in a line width (FWHM) of 0.144 ± 0.007 cm-1 at 760 Torr and 285K.

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I. INTRODUCTION

PURPOSE

With the advent of semi-conductor lasers and their recent application to spectroscopy [2,16,17,22], there has been a revolution in the study of infrared spectra. Use of the tunable diode laser (TDL) has permitted ultra high resolution ($<0.0001 \text{ cm}^{-1}$) studies to be performed for several atmospheric constituent molecules of high current interest (ClO , HNO_3 , SO_2 , CF_2Cl_2 , etc.) [2,17,37]. This study is concerned with the experimental determination of pressure broadening characteristics of a single ozone absorption line near 1129.4 cm^{-1} , utilizing a TDL as a radiation source.

The shape of any spectral line contains information which is indicative of the conditions existing in the vicinity where the absorption or emission of radiation takes place. Consequently, spectral analysis of the factors which contribute to the finite width, strength, and position of an observed line leads to a determination of temperatures, pressure, concentrations, and species of the source molecules, even while existing in extraordinarily small

amounts or at extreme distances. Remote sensing techniques such as heterodyne radiometry and differential lidar have been developed [16,22] in the application of calculating atmospheric transmittance. These systems are designed to retrieve high resolution spectral line profiles, from which by means of analytical inversion methods, it is possible to infer concentration and temperature profiles of atmospheric constituents. Most of these techniques operate in spectral regions where the molecular species of interest exhibits a strong absorption coefficient and absorption by interfering species is minimal. In order to produce accurate results, a precise knowledge of spectral line parameters is required.

A high resolution ground observation infrared Fourier Transform spectrogram of solar spectra around 8.85 microns by Goldman et.al. [12] is shown in figure 1. An indicator marks the ozone vibration rotational transition $(v_1, v_2, v_3, J, K_A, K_C)$ $(1, 0, 0, 31, 1, 31 \leftarrow 0, 0, 0, 32, 0, 32)$ centered at 1129.426 cm^{-1} (8.85406 microns). This line is a good candidate for use in the remote sensing of ozone since it meets the criteria with respect to windows, strength and favorable ground state.

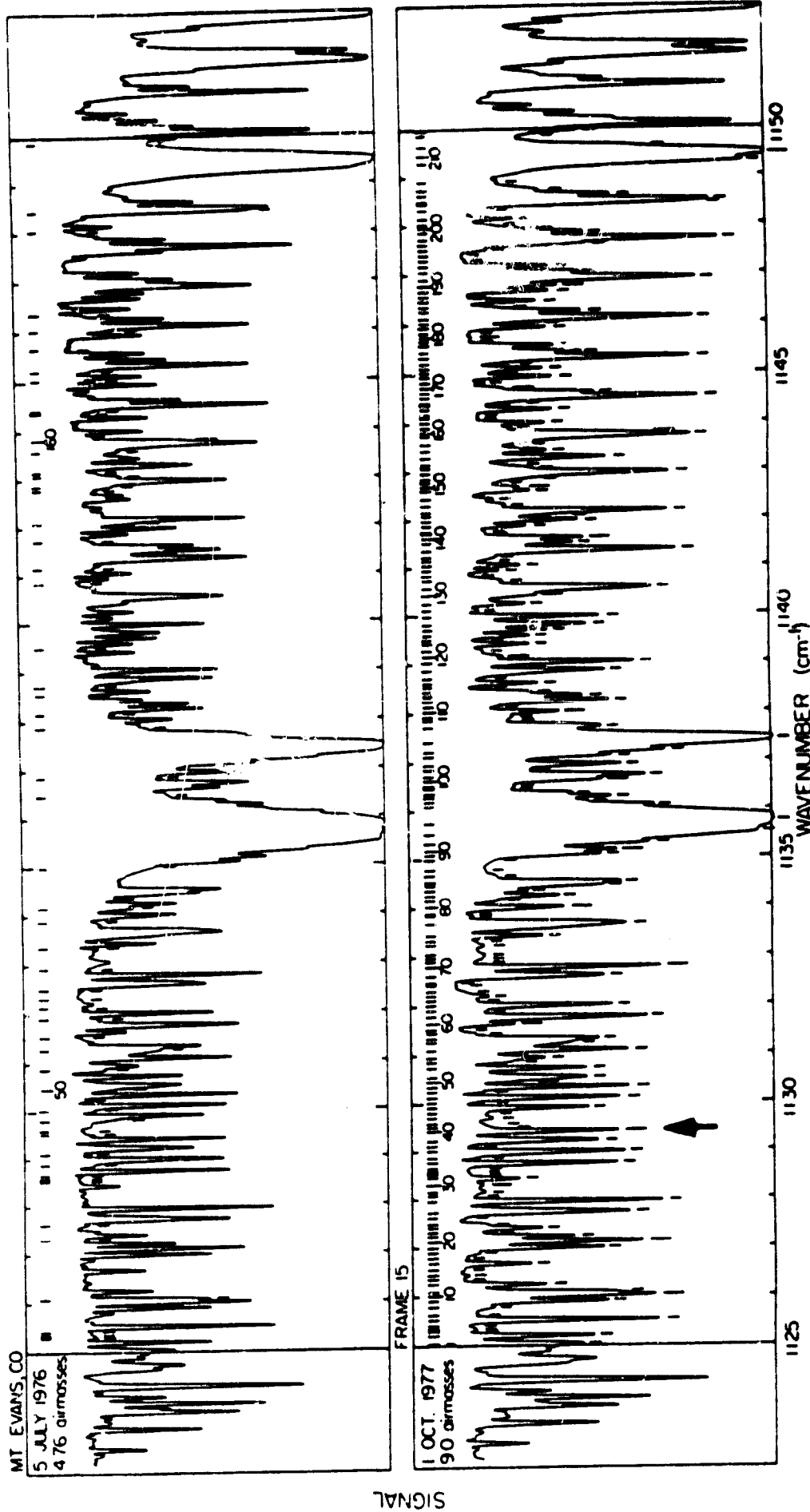


Figure 1. High resolution solar spectra at high and low sun.

The subject of this thesis is an experimental investigation of this line which results in a determination of the absorption coefficients from which "independent" values of line strength, Lorentz self pressure broadened halfwidth, Doppler width, and ozone - ozone collision cross section are found. In addition we will explore some of the physical phenomena that contribute to spectral line broadening and the experimental method used to measure spectral line parameters.

REVIEW OF RESEARCH

A survey of relevant ozone line parameters available to date (mid 1980) is presented in Table 1. [15]. Column 1 of the table lists the author; column 2 the spectral range; column 3 whether band model parameter or single line parameter; columns 5,6,7, and 8 list values for half-width at half absorption maximum, α , for ozone-ozone, ozone-oxygen, ozone-nitrogen and ozone-air broadening, respectively. Column 9 indicates whether it was an experimental (e) or theoretical (t) determination.

TABLE ONE
SUMMARY AND COMPARISON OF OZONE HALF-WIDTH DETERMINATIONS

1 Authors Date Reference	2 Spectral Region	3 Band Model y/n	4 Temper- ature Kelvin	5 O3-O3	6 Ozone Half-widths (cm-atm)-1	7 O3-N2	8 O3-Air	9 Type t/e
Tejwani (1975) [41]	MW (GHz) ? ? ? ?	n n n n	300. 300. 200. 200.	0.113 0.110 -- --	0.0411 0.2362 0.0538 0.0474	0.0752 0.0640 0.0991 0.0861	0.068 0.058 0.0986 0.0780	t t t t
Walshaw (1975) [45]	IR (cm-1) 1000- 1060	y	293.	--	--	--	0.078	e
Goldman (1970) [11]	IR (cm-1) 955- 1180	y	235.	--	--	--	0.085	e
Lichtenstein (1971) [29]	MW (GHz) 110- 118	n	293.	0.117	--	--	--	e

TABLE ONE
(Continued)

1 Authors Date Reference	2 Spectral Region	3 Band Model y/n	4 Temper- ature Kelvin	5 O3-O3	6 Ozone Half-widths (cm-atm)-1	7 O3-N2	8 O3-Air	9 Type t/e
MCAfee (1975) [31]	IR(cm-1) 1054	y	298.	--	0.070	--	--	e
Aida (1975) [1]	IR(cm-1) 1050	n n	293. 250.	-- --	-- --	-- --	0.082 0.093	t t
Menzies (1976) [34]	IR(cm-1) 1054 1049 1043 1043 1043	n n n n n	298. 298. 298. 298. 298.	-- -- -- -- --	0.0935 0.098 0.09 0.10 0.08	-- -- -- -- --	0.105 0.121 0.10 0.12 0.10	e e e e e
Monnanteuil (1980) [35]	MW(GHz) 76.533 77.602 93.955 96.228 96.228	n n n n n	292. 292. 292. 292. 245.	0.124 0.119 0.127 0.111 0.139	-- -- -- -- --	-- -- -- -- --	-- -- -- -- --	e e e e e

From an examination of table 1, it is apparent that:

- 1.) Only 2 experimental determinations of O_3-O_3 broadening, have been reported, both at microwave wavelengths.
- 2.) No O_3-N_2 measurements have been reported in any spectral region.
- 3.) No direct measurements in the infrared have been made.

The early low resolution study by Walshaw 1954 [45] estimated average air broadened linewidths in the ν_3 fundamental band to be $.078 \text{ cm-atm}^{-1}$ (HWHM) at 20°C . This "independent" value has been used as a standard, implicitly or explicitly, by many later workers.

The millimeter wave spectrum of ozone has since been observed by Lichtenstein et. al. 1971 [29] and produced the only experimental measurements of individual linewidths until this year (1980). They reported self-broadened linewidths for two transitions at 118.4 GHz (J, K_a, K_c) = $(1,1,1 \leftarrow 0,0,0)$ and 110.8 GHz ($6,1,5 \leftarrow 6,0,6$) yielding an average halfwidth of $4.63 \pm .24 \text{ MHz/Torr}$ ($.117 \text{ cm}^{-1}/\text{atm}^{-1}$) (HWHM). The exact experimental situation is unclear from their paper, however, and thus leaves some question as to the purity and pressure of the ozone in their work.

Tejwani and Yeung 1975 [41] present a theoretical calculation of O_3-O_3 , O_3-O_2 , O_3-N_2 and O_3 -air linewidths based on Tsao-Curnutte-Anderson theory for both A and B type bands. The average self broadened HWHM value for type A and

B bands was found to be .1128 cm⁻¹ atm⁻¹ and .1104 cm⁻¹ atm⁻¹ respectively. From their tabulation it is seen that " α O₃-O₃ show quite appreciable variation with respect to quantum numbers." The broadening parameter value obtained by this calculation depends in part on the quadrupole moment adopted for O₃ which is not well known. Their method was to use a value which gave the closest fit to the experimental data of Lichtenstein et. al. [29]. Not surprisingly therefore, the data agrees well with Lichtenstein's and so the result is not independent. It is the Tejwani-Yeung average halfwidth value that is currently listed on the AFCRL line parameters compilation [32].

Recently, Monnanteuil 1980 [35] has reported privately unpublished values for O₃O₃ of 5 microwave transitions listed in table 1. Details of the study, however, are not available at this time.

II. THEORETICAL FORMULATION

INFRARED SPECTROSCOPY - DEFINITIONS

The theory and application of direct absorption spectroscopy is discussed in many references [6,14,18,42,43] to which the reader is referred for detailed development. However, in order to introduce and define some important concepts used here, the spectroscopic procedure and theory are briefly outlined below.

1. Transmittance

Basically, as radiation of intensity $I_0(\nu)$, incident on a transparent cell containing a gaseous sample of the molecule of interest is "tuned" in frequency, absorption of the radiation will occur at discrete frequencies which give rise to the molecular spectrum. At these frequencies the portion of the radiation absorbed is governed by the strength of the particular line. The ratio of incident intensity, $I_0(\nu)$, to the intensity that passed through the cell, $I(\nu)$, is defined as the transmittance (T). A typical plot of the transmission function over a single line may

appear as in our result (figure 11). The line center (ν_0) is the point in frequency where the transmittance is least (maximum absorption).

2. Absorption Coefficient

The transmittance is proportional to the concentration of molecules in the cell and is given by Beers' law (sometimes referred to as the Lambert - Bouguer law) given by:

$$T(\nu) = I(\nu)/I_0(\nu) = \exp(-k(\nu)lp) \quad (1)$$

where l is the path length of absorption, p is the partial pressure, of the absorbing gas, and $k(\nu)$ is the absorption coefficient evaluated at the frequency, ν . Figure 12 is a plot of the absorption coefficient which gives rise to the transmittance shown in figure 11. Commonly, a parameter used to quantify this profile is the full width at half maximum intensity (FWHM) designated by α . This parameter has special significance with respect to the lifetime of the excited state. Another parameter used to describe the profile is the integrated line strength and is defined as the integral of the absorption coefficient with respect to frequency.

3. Units

As a matter of reference, frequency or wavelength is customarily given in units that are contingent on the spectral region of interest. In the infrared, spectroscopists often use the wavenumber (ν'), rather than wavelengths. Wavenumber is the number of waves per unit length, i.e. the reciprocal of wavelength. The units are expressed in reciprocal centimeters (cm^{-1}), while wavelengths are in units of microns (μ) where $1\mu = 1 \times 10^{-20}$ $\text{cm} = 10,000 \text{ cm}^{-1}$. Another name for the cm^{-1} is the Kayser, the relation being, 1 millikayser (mk) = $1 \times 10^{-3} \text{ cm}^{-1} = 30 \text{ MHz}$.

THE OZONE MOLECULE

Ozone is a minor constituent of the earth's atmosphere existing in concentrations on the order of a few ppm in a tenuous layer 5 to 10 km thick at an altitude of about 30 Km in the stratosphere. It plays an extremely important role in radiative transfer and in the photo-chemical cycles of the atmosphere. The molecule has several absorption bands in the ultraviolet ($\lambda < 300\text{nm}$) that are responsible for filtering approximately 99% of the radiation that would otherwise reach the earth's surface. Most of this is due to the Hartley absorption band which consists of a strong

continuum between 300 and 220 nm with a very high and almost symmetrical peak near 255 nm [19].

This triatomic, non-linear molecule is a slight asymmetric top ($I_a \neq I_b \neq I_c$) with C_{2v} symmetry and an apex angle of 116.8° [44]. Its symmetry and three fundamental vibrational modes are illustrated in figure 2.

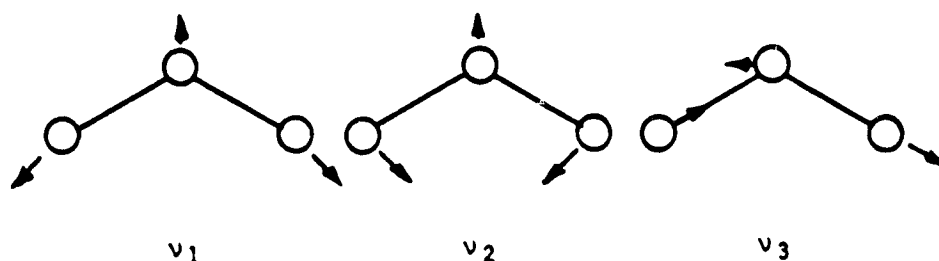


Figure 2. Normal vibrational modes of the ozone molecule.

The resulting spectra of ozone as any asymmetric molecule is fairly complex. Ozone is a slight to weak dipole having a dipole moment of 0.53 debye (0.53×10^{-18} esu) [44]. From microwave studies [36] fundamental rotational constants are determined to be:

$$A = 106,534.74 \text{ MHz}$$

$$B = 13,348.95 \text{ MHz}$$

$$C = 11,834.30 \text{ MHz}$$

The rotational constants are defined as $A = h/8\pi^2 I_a$,

$B=h/8\pi^2I_b$, $C=h/8\pi^2I_c$, where h is Planck's constant and I_a , I_b , I_c , are the inertial moments about the corresponding axes. From these constants, vibrational rotational band centers have been designated by Kaplan et.al. [28] as:

$$\nu_1 = 1110 \text{ cm}^{-1}$$

$$\nu_2 = 705 \text{ cm}^{-1}$$

$$\nu_3 = 1042.2 \text{ cm}^{-1}$$

These moments of inertia yield a value of -0.97 for Ray's asymmetry parameter (K), defined as:

$$K = \frac{(2B - A - C)}{A - C}$$

Thus, for the ground state, this molecule is very nearly a prolate symmetric top.

The small binding energy (Dissociation energy of 1.04 eV [19]) accounts for the extreme reactivity so characteristic of this most oxidizing of all molecules. This fact has hindered extensive study of high pressure ozone due to the imposing problems of purification and explosive hazard.

THEORY OF LINEWIDTHS AND SHAPES

The spectral profile of figure 11 is fundamental to our study. It is actually a convolution of several separate broadening processes. They are the natural, Doppler, and collisional lineshapes that are observed together and are referred to as the Voigt shape. Each is briefly considered below.

1. Natural Lineshape

The natural or radiative lineshape is a direct consequence of the finite lifetime of an atomic or molecular energy state. It can be viewed either in a classical sense or quantum mechanically, both yielding the same result.

Classically, we can picture the system as a bound harmonic oscillator damped by virtue of its own radiation [6,27]. A good approximation of the equation of motion for the oscillating electron is given by:

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = 0 \quad (2)$$

where:

$$\gamma = \frac{e^2 \omega_0^2}{6\pi \epsilon_0 c^3 m}$$

is the classical decay rate and ω_0 = resonant angular frequency.

For $\gamma \ll \omega_0$, Equation (2) has solution:

$$x = x_0 \exp(-\gamma t/2) \exp(-i\omega_0 t) \quad (3)$$

which has the form of a damped oscillation. The electric field can be determined through Maxwell's equations to be:

$$\begin{aligned} E(t) &= E(0) \exp \left\{ -i(\omega_0 - \frac{i\gamma}{2})t \right\} & t \geq 0 \\ E(t) &= 0 & t \leq 0 \end{aligned} \quad (4)$$

which are similarly time dependent. Since the wave train is not infinite, it is not truly monochromatic and can therefore be resolved into its component frequencies by taking the Fourier transform:

$$E(\omega) = \left(\frac{1}{2\pi} \right)^{1/2} \int_{-\infty}^{\infty} E(t) \exp(i\omega t) dt \quad (5)$$

The intensity or power distribution, $I(\omega)$, is proportional to $E(\omega)^2$ and so is found to be:

$$I(\omega) = I_0 \frac{\gamma/2\pi}{(\omega - \omega_0)^2 + \gamma^2/4} \quad (6)$$

or in terms of frequency:

$$I(\nu) = I_0 \frac{(\gamma/4\pi)^2}{(\nu - \nu_0)^2 + (\gamma/4)^2} \quad (7)$$

where I_0 is the maximum intensity at the line center frequency ω_0 , or ν_0 , and

$$\gamma = \frac{1}{\tau_{cl}} = \frac{1}{\text{classical lifetime}} \quad (8)$$

This important functional form, (6) or (7), is called a Lorentzian distribution and is the natural lineshape. It is illustrated in figure 3. The linewidth FWHM is given by,

$$\alpha = \gamma = 1/T_{\text{classical}} = 2\pi\Delta\nu \quad (9)$$

Quantum mechanically the same result can be obtained in a simple manner by an application of the uncertainty principle:

$$\Delta E \Delta t \geq \hbar \quad (10)$$

Δt is the time uncertainty that an atom will spend in an excited state and is measured by the mean lifetime of the state. ΔE is the corresponding energy uncertainty of the level, which is,

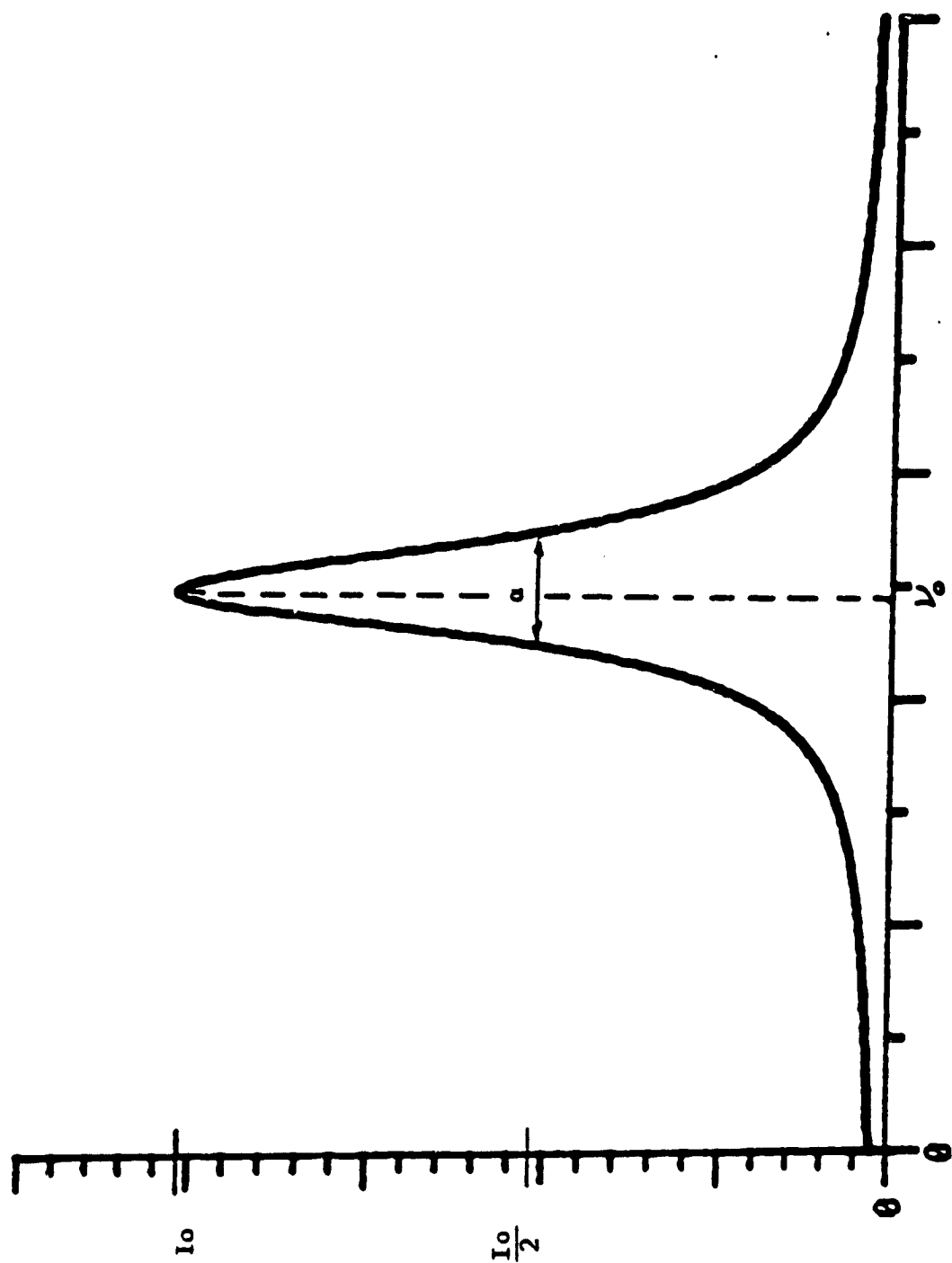


Figure 3. Lorentzian line profile. The half width is given by $a = \gamma/2\pi = 1/2\pi \tau_{\text{class}}$.

$$E = h \nu$$

or

$$\Delta E/h = \frac{h \Delta \nu}{h/2\pi} = \Delta \nu 2\pi$$

So the frequency spread of a particular state, say j , can thus be written:

$$\Delta \nu_j = \frac{1}{2\pi \tau_j} \quad (11)$$

which compares to equation (9). Actually one should use an uncertainty of $\nu = \nu - \nu + \nu$, but is negligible for the ground or metastable state since $\tau \rightarrow \infty$.

The lifetime of an excited state is related to the transition probabilities by,

$$\tau = 1/\sum A_{ji} \quad (12)$$

if more than one transition is possible. It can be shown [42] (in MKS units) that A_{ji} is proportional to ν^3 by:

$$A_{21} = \frac{4\pi^3 \nu_0^3}{3 \epsilon_0 c^3 h} P_{ox}^2 \quad (13)$$

where P_{ox}^2 is the dipole moment matrix element. Consequently natural line width decreases rapidly in the infrared. A comparison of the magnitude of natural widths in the infrared to optical frequencies can be gained using

(11), (12), and (13), i.e.

$$\Delta\nu = \nu^3 \quad (14)$$

Halfwidth of a transition at ten microns compared to one at say .5 microns is approximately four orders of magnitude smaller. Natural width in the infrared will normally be several orders of magnitude less than Doppler or collision broadened width.

2. Doppler Broadening

In the regime of low gas pressure the observed linewidth is due primarily to the Doppler shifting of emitted or absorbed frequencies due to thermal motion of the molecules. Molecules moving with a component of velocity away from the observer give rise to a red shift and conversely those moving towards, shift blue. Since the shift varies from one molecule to another the effect is not the same for all molecules and therefore classified as an inhomogeneous broadening mechanism.

The observed shifted angular frequency is given by,

$$\omega'_0 = \omega_0 (1 - \vec{v} \cdot \vec{r}/c) \quad (15)$$

where \hat{r} is a unit vector in a direction from the observer to the molecule and ω_0 is the emitted or absorbed frequency of the stationary atom.

Statistically the probability of an atom having a velocity between v and $v+dv$ in a one dimensional coordinate system is given by the Maxwellian distribution,

$$P(v)dv = \left(\frac{M}{2\pi kT} \right)^{1/2} \exp \left(- \frac{Mv^2}{2kT} \right) dv \quad (16)$$

where,

M = Mass of the atom

T = absolute temperature

k = Boltzman's constant

Let the line width parameter, Δ , be defined by

$$\Delta = 2 \frac{\omega_0}{c} \left(\frac{2kT}{M} \right)^{1/2} \quad (17)$$

then from (15), (16), and (17) the probability of absorbed or emitted radiation having an angular frequency between ω_0' and $\omega_0' + d\omega_0'$ is given by,

$$P(\omega_0')d\omega_0' = 2/\Delta\pi^{1/2} \exp \left\{ -4(\omega_0' - \omega_0)^2/\Delta^2 \right\} d\omega_0' \quad (18)$$

This form of the profile is a Gaussian distribution (due to the Maxwellian velocity distribution), about the central

frequency ω_0 : whose width (FWHM) is given by,

$$\alpha_D = \Delta(\ln 2)^{1/2} = 2 \frac{\omega_0}{c} \left(\frac{2kT}{M} \ln 2 \right)^{1/2} = 7.16 \times 10^{-7} \omega_0 \left(\frac{T}{A} \right)^{1/2} \quad (19)$$

Compared to the Lorentzian function, the Gaussian drops off rapidly on either side of its center, (see figure 5). In fact, 99.994% of the area under the curve is contained within the bounds of \pm four linewidths. The Doppler width in terms of wavelength is given by

$$\alpha_D = 7.16 \times 10^{-7} \lambda \sqrt{T/A} \quad (20)$$

It is apparent that α_D varies linearly with wavelength. For the ozone molecule, ($A = 48$), at a temperature $T = 300K$, one finds in the ultraviolet (10nm), the Doppler width is approximately 1.8×10^{-5} nm which is on the order of the natural width. In the infrared ($\approx 10\mu$) the Doppler width of ozone is approximately 60 MHz, two orders of magnitude greater than the natural width. Observed spectra in this experiment is Doppler limited.

3. Collision Broadening

In all real physical situations of interest a molecule is not alone in the universe, and so will consequently be subjected to interactions by neighboring atoms, ions, or electrons, which in turn perturb the molecular energy levels. For a large collection of such events averaged over many molecules, broadening of its spectral lines is observed.

The first successful qualitative collision theory was formulated by Lorentz [30] in seeking explanations of absorption experiments by Angstrom and Halls. He envisioned the excited electron oscillating with a subsequent field $f(t)$ and assumed that the perturbation due to the interaction of a colliding molecule quenched the radiating wave train abruptly. Disregarding the relatively small radiation damping, a Fourier analysis of $f(t)$ similar to that for the natural broadened line yields the power distribution illustrated in figure 4b. For many collisions, averaging over all possible values of t , produces the Lorentzian profile:

$$I(\omega) = I_0 \frac{(1/\tau)^2}{(\omega - \omega_0)^2 + (1/\tau)^2} \quad (21)$$

shown in figure 4c, where τ is the mean time between collisions and the FWHM $\alpha_L = 2/\tau$.

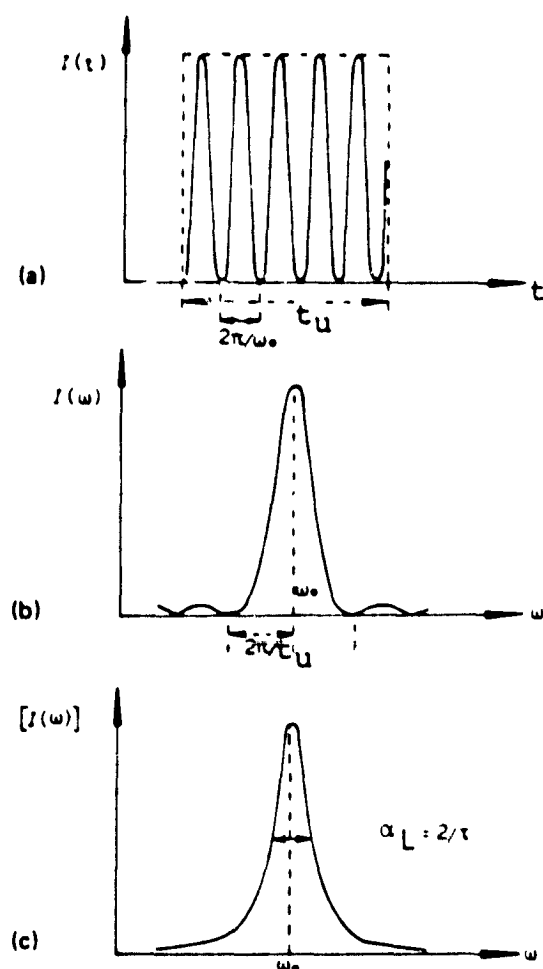


Figure 4. Effect of abrupt cut-off of radiation. (a) shows the rectangular cut-off function of duration t_u . (b) shows the frequency spread resulting from the cut-off of width $2\pi/t_u$. (c) shows the Lorentzian distribution obtained by averaging (b) over all possible values of t_u . τ is the mean value of t_u .

This method of calculation is termed the impact approximation and assumes that the duration of a collision is small compared to the time between collisions. This result is used in many cases to describe line broadening below 100 Torr. Collision theory has since been extended to include other effects: phase changes on impact [46,47]; density of perturbers; long and short range forces, and other mechanisms of interaction.

Compared to the Doppler profile, the Lorentzian distributes more energy away from the spectral center. Consequently, pressure effects are dominant in the wings of the line.

The mean time between collisions, T_c , in terms of the mean free path is found from kinetic gas theory to be,

$$T_c = \lambda / \bar{v} \quad (22)$$

The mean relative velocity, \bar{v} , is given for a Boltzman distribution of like collision partners as:

$$\bar{v} = 4 \sqrt{\frac{kT}{\pi m}} \quad (23)$$

Thus, the linewidth, α_L , is given by

$$\alpha_L = \frac{2}{T_c} = 2N\sigma\bar{v} \quad (24)$$

where N is the number density and σ is the collision cross section.

4. The Voigt Profile

In almost any absorption experiment, the observed lineshape will not be a simple Lorentzian or Gaussian, but a convolution of the two called the Voigt profile. It is derived by averaging the Lorentz function (equation 21) over the thermal distribution of equation 16, resulting in the probability distribution $P(x,y)$, (normalized to unity over $v-v_0$), given by Armstrong[3]:

$$P(x,y) = \frac{1}{a_D} \sqrt{\frac{\ln 2}{\pi}} K(x,y) \quad (25)$$

where $K(x,y)$ is given by:

$$K(x,y) = \frac{k_v}{k_0} = \frac{y}{\pi} \int_{-\infty}^{+\infty} \frac{\exp(-t^2)}{y^2 + (x - t^2)} dt \quad (26)$$

and is known as the Voigt function. $K(x,y)$ is a reduced absorption coefficient, where:

$$k_0 = \frac{S}{a_D} \sqrt{\frac{\ln 2}{\pi}} \quad (27)$$

equals the dimensional constant of the reduced absorption

coefficient. S , is the integrated line strength given by:

$$S = \int_{-\infty}^{+\infty} k_{\nu} d\nu \quad (28)$$

It is commonly expressed in units per absorbing molecule (cm-1/molecule cm-2).

$$x = \frac{\nu - \nu_0}{\alpha_D} (\ln 2)^{\frac{1}{2}} \quad \begin{array}{l} \text{(wave number scale in units} \\ \text{of Doppler width HWHM)} \end{array} \quad (29)$$

$$\alpha_D = \nu_0 \left(\frac{2kT \ln 2}{Mc^2} \right)^{\frac{1}{2}} \quad \begin{array}{l} \text{(Doppler half width HWHM)} \end{array} \quad (30)$$

where ν_0 is the wave number at line center and ν is the wave number at which K_{ν} is to be evaluated.

The shape of this profile is determined by the ratio of Lorentz to Doppler widths, designated here as y , where

$$y = \frac{\alpha_L}{\alpha_D} (\ln 2)^{\frac{1}{2}} \quad (31)$$

It is this parameter that will be evaluated from the experimental data. Unfortunately, the Voigt profile cannot be expressed in a concise analytic form, but it can be evaluated numerically. It has been tabulated by several authors [7,10,25,8] whose results have been utilized by others to fit the observed profiles.

Figure 5 illustrates the contribution of the Doppler and Lorentz profiles to the Voigt for the case of $\alpha_L/\alpha_D = (\ln 2)^{1/2}$. A change in the ratio quantifies the dominance of one case over the other. Physically "pure" cases are not observed. In the limits of the ratio however, it should be noted that the shape reduces to the independent broadening formula; i.e. for the "pure" Doppler regime, as $\alpha_L \rightarrow 0$, $K(x,0) \propto \exp(-x^2)$; similarly for "pure" Lorentz as $\alpha_D \rightarrow 0$,

$$P(x \rightarrow \infty, y \rightarrow \infty) \quad x/y = \frac{(v - v_0)}{\alpha_L} = \frac{1}{\pi} \frac{\alpha_L}{(v - v_0)^2 + \alpha_L}$$

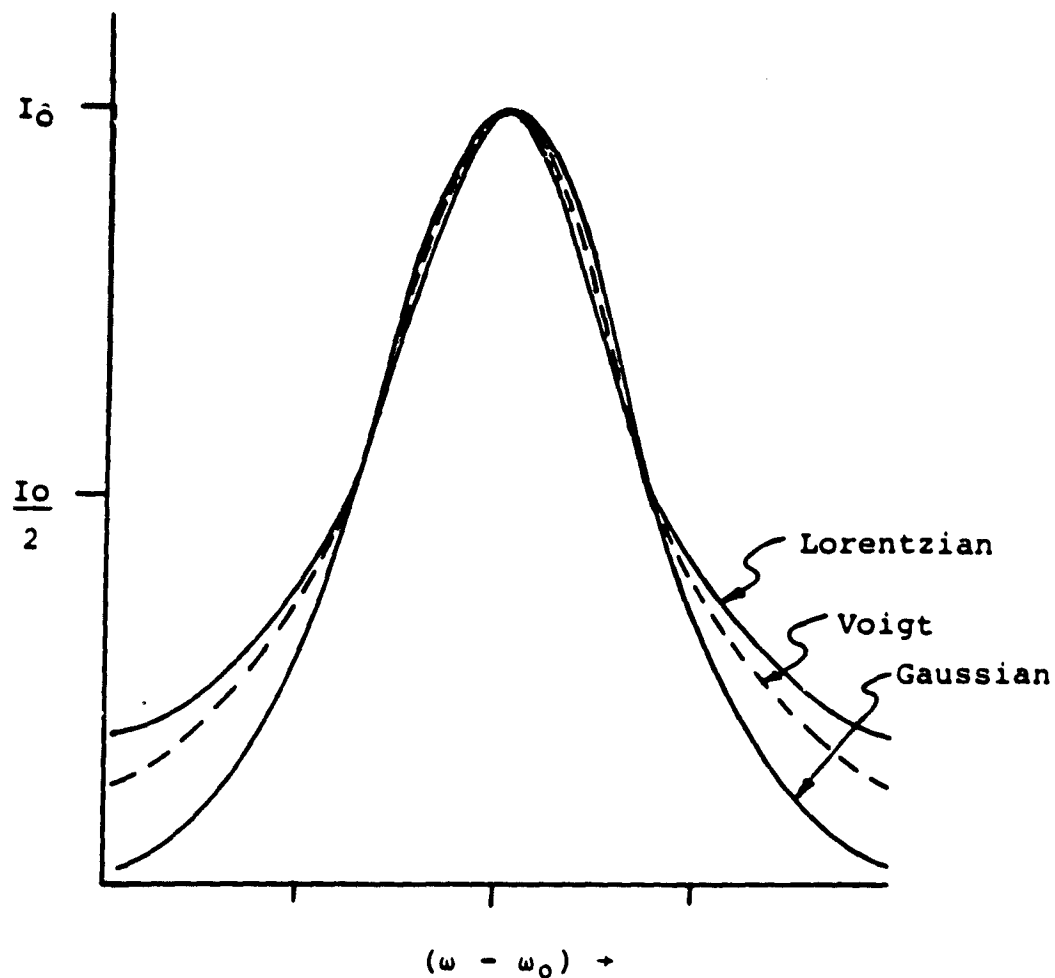


Figure 5. Comparison of the shapes of the Lorentzian distribution, the Gaussian distribution, and the Voigt line profile. $\alpha_L/\alpha_D = (\ln 2)^{1/2}$ and profiles are normalized to the same peak intensity and halfwidth.

III. EXPERIMENTAL APPARATUS AND PROCEDURE

TUNABLE DIODE LASERS

The radiation source used in this experiment was a PbSnSe diode laser manufactured by Laser Analytics, Inc. graciously made available by the Laser Spectroscopy Branch, NASA Langley Research Center. Extensive use of tunable diode lasers (TDL) for this type of application has been made since the first publication in 1970 of Doppler limited spectra within the 10.6 micron band of SF₆ [20]. An excellent review of these devices is presented by Butler [5].

The semiconductor laser is mounted on an oxygen-free copper cold head which is cooled by a closed cycle Helium refrigerator, manufactured by CTI - Cryogenics Helix, Waltham, Ma. A forward bias applied to the diode produces emission at a wavelength determined by the energy gap of the semiconductor. Total output power is typically about one milliwatt continuous wave.

There are two main aspects which make the application of this type of device to spectroscopy advantageous. First, their unprecedented narrow line width (<10 MHz) is orders of magnitude narrower than conventional prism instruments. The high resolution virtually eliminates instrumental width limitations [40] permitting essentially undistorted measurements of individual line profiles so that pressure broadening studies can be carried out by direct linewidth measurements. Secondly, they are tunable in a piecewise fashion through most of the infrared (three microns to thirty microns). Tuning can be accomplished in several ways: varying the diode temperature, applying a magnetic field, applying external pressure, or sweeping the current through the semiconductor. A practical arrangement used here, was to stabilize the diode temperature at approximately 37° K and vary the current linearly with time (at a sweep rate of 2.0×10^{-4} Amp/sec) from 1.0630 to 1.0839 Amps (≈ 20 ma change) with a corresponding frequency sweep of approximately $.12 \text{ cm}^{-1}$ (3.6 GHz).

EXPERIMENTAL ARRANGEMENT

A schematic of the TDL spectroscopy apparatus is shown in figure 6. The laser's output radiation was collected by a germanium $f/1.5$ lens, chopped, and passed through a

TDL SPECTROSCOPY FACILITY

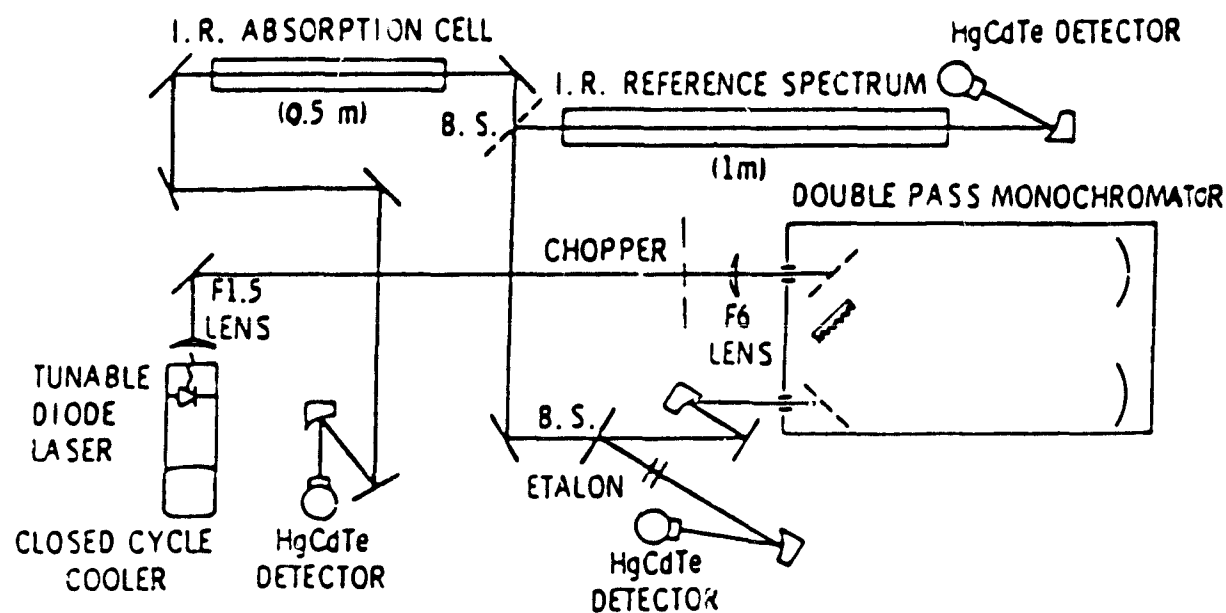


Figure 6. Optical setup for simultaneous measurement of reference gas spectrum, test gas spectrum and etalon tuning curve.

Czerny-Turner double pass monochromator to isolate one of several longitudinal modes normally emitted by these lasers. The output from the monochromator is divided by a beam splitter which directs 40% through a solid 5.08 cm germanium etalon and is focused on a LN₂ cooled HgCdTe detector [26]. The transmission signal through the etalon provides a calibration scale to convert the laser current scale into relative wavenumbers, providing the free spectral range (FSR) is some small fraction of the tuning range of the mode. In this case the FSR is .02445 cm⁻¹. In addition, this signal may be used to monitor the laser tuning characteristics which are often complicated by effects such as mode hopping, multimode output, and non-linearities [16]. The remaining 60% is directed to another beam splitter which directs a portion of the beam through a reference cell on to another detector. This cell contains SO₂ at a pressure of one Torr as a reference gas, whose spectrum in this region is precisely known [21,39]. An accurate determination of wavelength can be made by measuring its separation from any of the reference lines. The remaining radiation passes through the 50 cm O₃ single pass absorption cell to a third detector.

Windows of the absorption cell were made of KCl 50 mm in diameter and 6.5 mm thick. Ozone pressure is measured by a 0-100 Torr Datametrics Barocell pressure sensor and electronic manometer.

This particular arrangement permitted simultaneous measurement of the ozone spectra, the reference gas spectra, and the etalon curve with the same laser sweep.

Figure 7 illustrates the signal processing path through a block diagram of the electronics. Output signals from the three detectors are passed through appropriate electronic filters, phase sensitive amplifiers, and then digitized using a 16 channel 12 bit ADC coupled to a PDP-8 minicomputer which records the data on 7-track tape for future processing. Simultaneously the data is monitored by an oscilloscope and a 2 channel Hewlett Packard chart recorder.

PROCEDURE

Ozone was generated from pure dry oxygen using the silent electrical discharge method [13], in a sealed glass system. The gas was condensed in a trap by liquid nitrogen (77K) and concentrated by pumping off excess oxygen. The cell was previously conditioned with ozone to minimize the effect of reactions with the cell walls, thus reducing impurities, and explosion potential.

Prior to producing ozone, a series of laser mode scans was performed to locate a strong, stable operational mode of the diode at the desired wavelength. The laser control

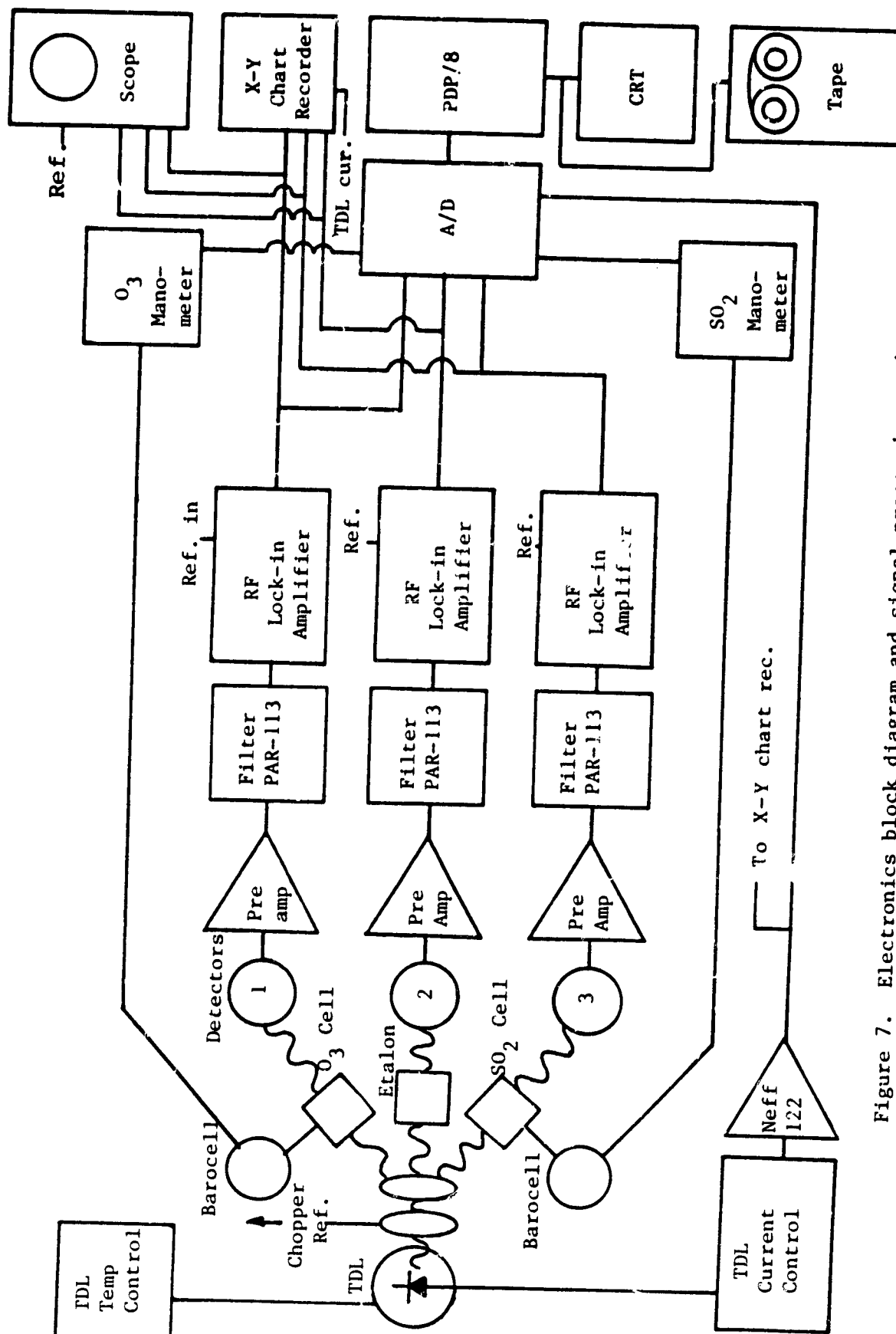


Figure 7. Electronics block diagram and signal processing path.

system is designed to automatically tune the laser over a predetermined frequency range once initiated.

The first scan was made with the laser's output blocked to determine an optical zero. The second scan is made through the evacuated absorption cell in order to record an unattenuated power curve (I_0) by which the following transmission curves are normalized. Ozone was then introduced into the cell at a pressure of 6.3 Torr and the first pressure scan is performed. Ozone is pumped from the cell for each successive scan reducing the pressure by approximately one Torr for each scan. This procedure was repeated for ten scans.

Throughout a scan, the amplified detector outputs, the TDL current, and the SO_2 and O_3 pressures were fed to the A/D converter and transferred to tape by the PDP-8. However, due to inconsistencies in the data tapes, (poor A/D performance) they were not used in the final data analysis. Instead the X-Y recording was digitized using a Numonics digitizer and recorded on magnetic tapes which were read into and stored on a Dec-system 10 for later analysis.

IV. DATA ANALYSIS

A series of Fortran programs were developed to efficiently reduce the spectroscopic data collected through the procedure described in the previous section and are included in Appendices A and B. The flow chart of figure 8 illustrates their sequence and purpose. The programs QUICK and VFIT perform the body of data analysis. They are interactive programs written for use on the DEC system-10 with tektronics graphics routines. Their important functions and organization are briefly described below.

PROGRAM QUICK

Program QUICK provides frequency calibration for the laser current array, and generates from the raw data an array of absorption coefficients from which the line parameters will later be determined.

The raw digitized data is organized into separate files consisting of the independent and dependent variables for each type of scan as illustrated in each curve of figure 9.

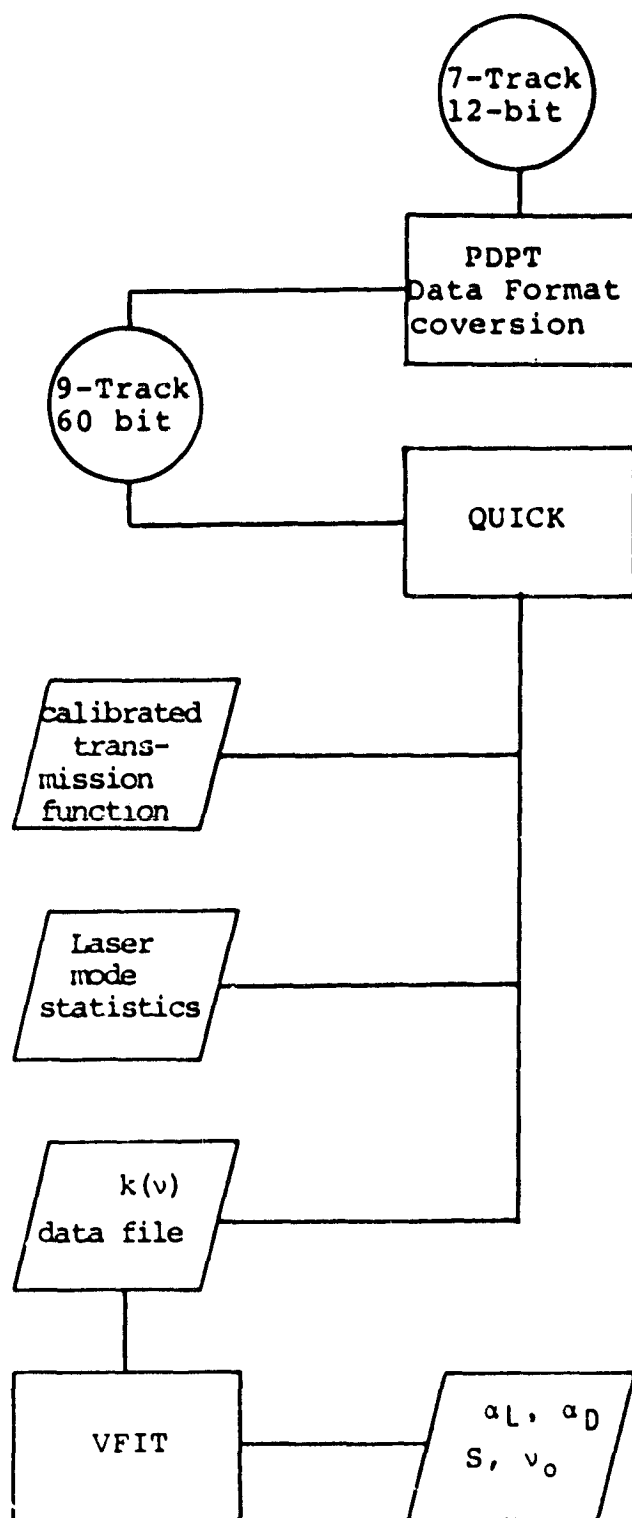


Figure 8. Data processing flow diagram illustrating sequence of analysis.

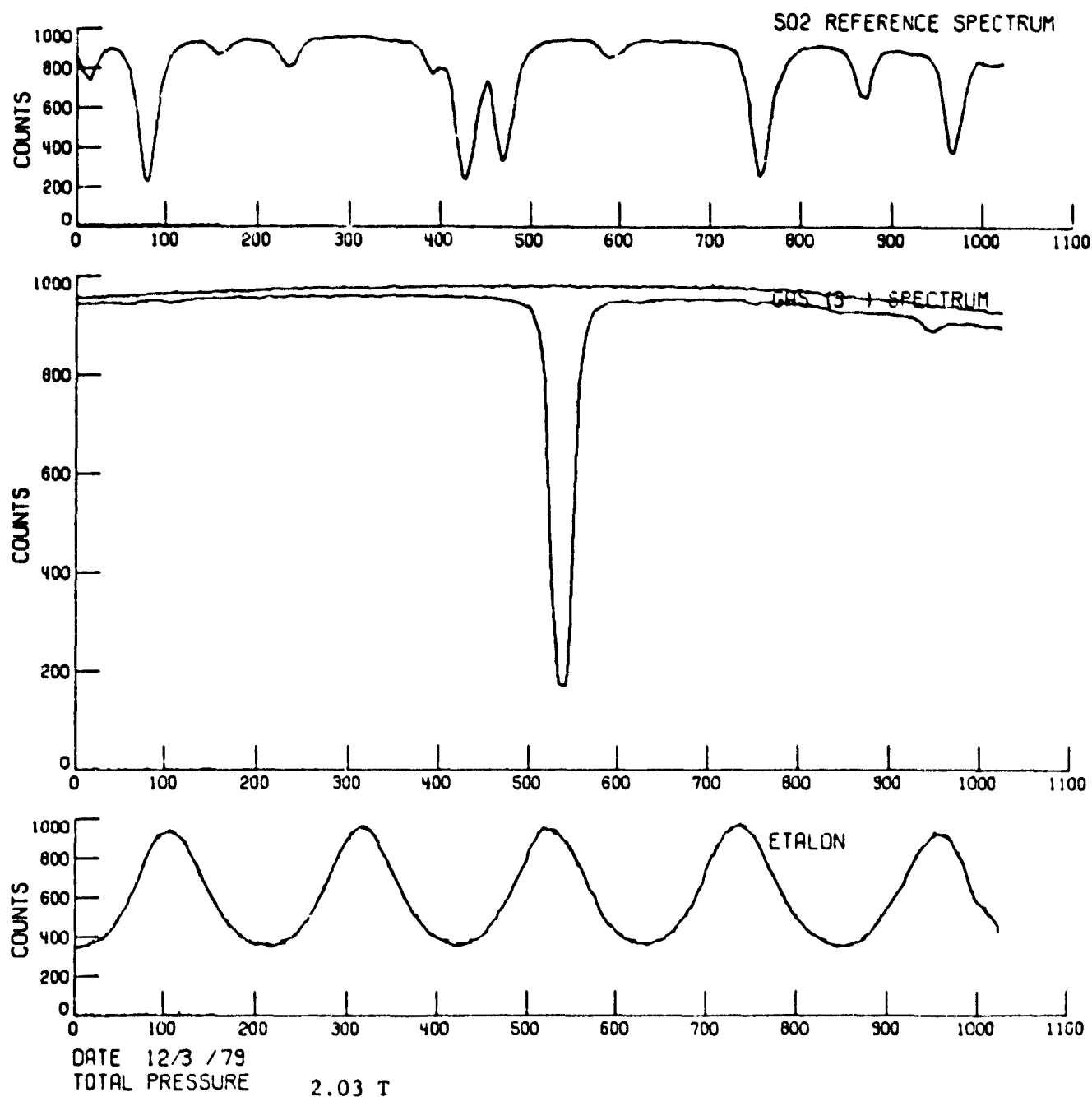


Figure 9. Uncalibrated raw data as collected by the PDP/8 minicomputer and recorded on seven track tape. The upper trace is the SO₂ reference spectrum. The middle traces represent the unattenuated power spectrum (I_0), and the 1129.426 cm⁻¹ ozone absorption line (I), at 2.03 Torr. The bottom trace is the etalon tuning curve.

The independent variable is always the laser current, CUR, in arbitrary units. The dependent variables are the detector signals. The detector signal through the empty cell is called EMPTY. The detector signal recorded with an optical path through the etalon is stored in the array ETALON. The signal corresponding to the optical zero is called ZERO, and the absorption cell or the reference cell signals are stored in the array GAS (the difference designated in the data file header record). Program QUICK is designed to perform all the calibration functions with the reference gas array first, then loop back and read in the absorption gas array (ozone) in its place to complete the analysis and thus the reason the GAS file will contain either the reference or the ozone gas data.

Immediately after reading each data file, subroutine CURFIT is called to "dress" the data before analysis. Here a cut off level is determined to eliminate portions of data with low S/N, as well as smoothing and alignment of the data arrays. Within this routine another subroutine, LINFIT, is called which by means of a linear least squares fit calculates and stores the slope and intercept of the current versus the location in the array. This provides a check on the linearity of laser current over time as well as an efficient way to store and manipulate the current array by reducing storage requirements from an entire array to only two numbers. Normalization is accomplished by dividing the

GAS curve by the EMPTY curve by use of the subroutine NORMAL.

Subroutine CNTFND is called to locate line centers (center minimums for absorption gas data and maximums for ETALON used later). This is done by numerically differentiating the entire gas curve and then determining where the derivative array passes through zero from positive to negative sense. Greater accuracy in location of line centers is gained by interpolation between the adjacent crossing points. An array of line center locations is passed back to the main program.

At this point a plot of the normalized reference data with marked centers can be produced, a sample of which is shown in figure 10 for SO_2 as the reference gas. This facilitates selection of a reference line for frequency calibration. The user is now asked to input the absolute frequency of the reference line.

In preparation for conversion of the current array to frequency the etalon trace is considered by subroutine ETPREP. After first smoothing the etalon trace the maximum intensity positions are determined by CNTFND. The change of current between peaks is calculated and stored in an array from which the average and standard deviation are derived. A plot of the etalon transmissions with marked maxima and a histogram of the fringe widths vs. their frequency of

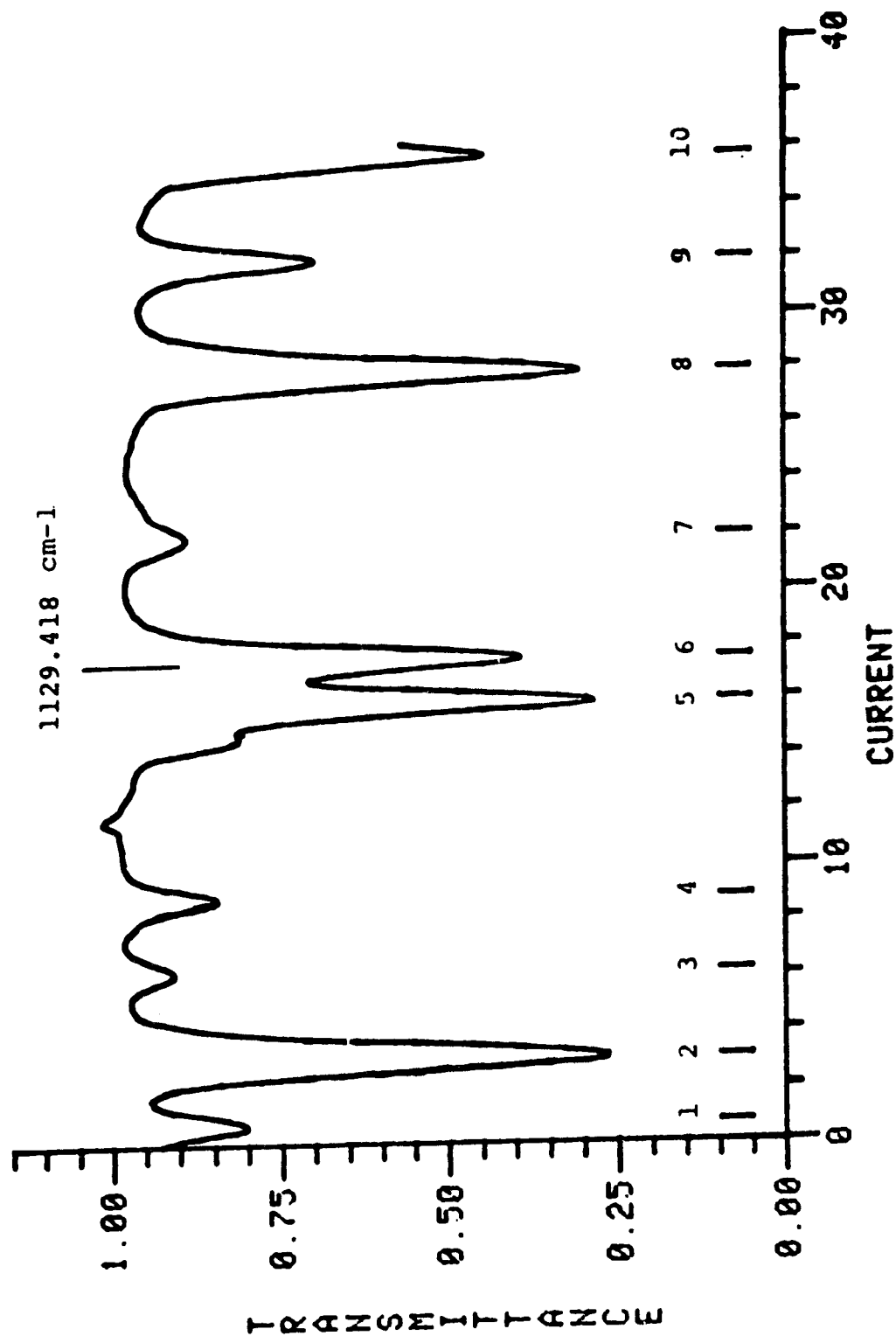


Figure 10. Normalized reference spectra (SO_2), over the frequency range of TDL scan, plotted by program QUICK. Marked are the line centers and center frequency of the selected reference line at 1129.418 cm^{-1} used for calibration (21,39).

occurrence may be generated from this subroutine. This process is important to detect subtle laser mode shifts and nonlinearities that can occur during operation of TDLs.

Conversion of the current array into absolute frequency is initiated by first transforming current to relative frequency (subroutine RELFREQ). A conversion factor is found by the ratio of the free spectral range of the etalon ($.02445 \text{ cm}^{-1}$ for our case) to the average fringe width previously calculated. Both the current and line center arrays are converted by multiplying each data value by the conversion factor. Transformation of this array to absolute values (ABFREQ) is determined by the difference between the absolute frequency value of the reference line and its value in the relative array just calculated.

A loop to the beginning of QUICK reads in the first ozone absorption curve as GAS which is then similarly chopped, smoothed, aligned and normalized. Since the current array is identical the calibration sections of the program are bypassed.

A normalized, calibrated plot of the ozone transmission function is generated, an example is shown in figure 11. An array of absorption coefficients is calculated using the Beer-Lambert law (equation one) and optionally appended to a data file for later processing by VFIT. Transmittances may also be appended to a separate data file. Data files

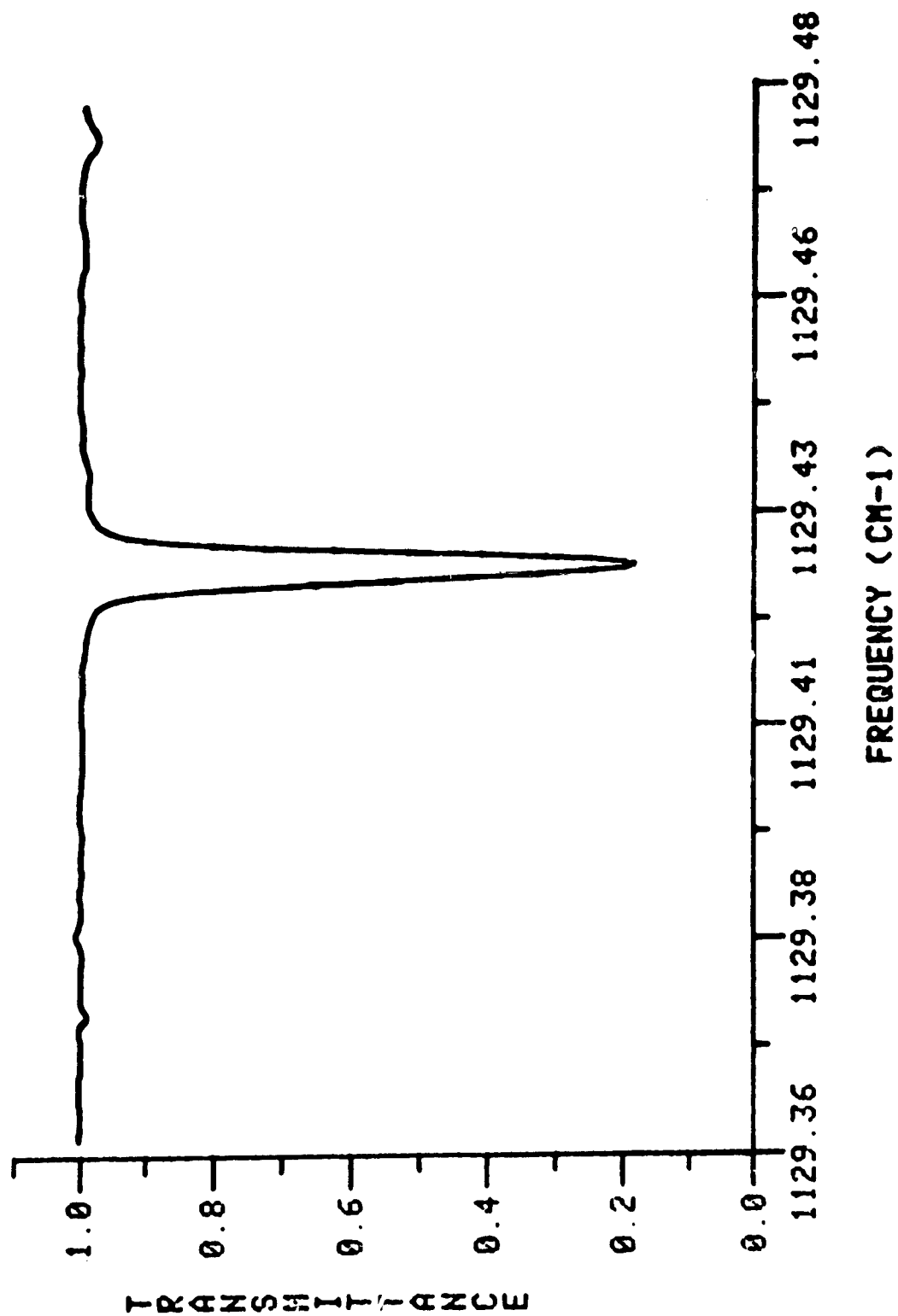


Figure 11. Transmittance of the ozone absorption line at 2.03 Torr and 285K after processing by program Quick.

remaining for different pressures may be succesively opened by QUICK and processed using the same calibration data.

PROGRAM VFIT

Program VFIT iteratively fits the Voigt function, $K(x,y)$ (equation 26), to the absorption coefficients $k(\nu)$ calculated in QUICK and produces estimators for the background signal, the center frequency of the absorption line, Lorentz and Doppler widths (HWHM), and the integrated line strength.

It utilizes the data files generated by QUICK. The spectral line center is determined by the maximum functional value of a parabolic fit to the line peak. This center frequency is removed from all data and the Doppler width (HWHM) is calculated (equation 30) for ozone at 285K. Next the program estimates from the data a first guess at the spectral line width and numerically integrates the absorption coefficient to obtain an estimator of the line strength. The data transformation is performed that converts the absorption coefficient versus frequency value to the reduced absorption coefficient (equation 26) as a function of frequency in Doppler units (x).

This observed profile is to be fitted to the function $K(x,y)$ - the Voigt profile with a fixed Doppler width. The function $K(x,y)$ is generated for given x,y values using the code described by Armstrong [3]. At line center ($x=0$), the value of the reduced absorption coefficient $K(0,y)$ is observed. That value is compared with a table of values of $K(0,y)$ generated by the function subprogram named K1. A linear interpolation is performed in the table of values of $K(0,y)$ to find the closest first guess for the value y (equation 31).

The value of y , as determined above, is increased by 25% and the reduced chi squared statistic is calculated for the data. This statistic is calculated for decreasing values of the parameter y in an iterative scheme until it is minimized. At this point the value of y , i.e. the ratio of the Lorentz to Doppler width is determined. A plotting routine is then called for displaying the data and the "best" fit (see figure 13).

Line strength is calculated over a symmetric interval about line center, determined by the number of data points above the 10% level of the peak. Wider lines are integrated over a proportionately wider data interval.

Minor functions of the program include data weighting options and background corrections.

V. RESULTS AND CONCLUSIONS

PRELIMINARY DATA SCREENING

The transmittance of the O_3 absorption line taken at 2.03 Torr and 285K is shown as figure 11 which is typical of the ten transmission curves after normalization and calibration. The 1129.418 cm^{-1} line of SO_2 ($v_1, v_2, v_3, j, k_a, k_c$) [1,0,0,33,3,31 \leftarrow 0,0,0,34,2,32] was selected as the standard reference line because of its proximity to the O_3 line under study and the recent heterodyne confirmation [39] of its position at 1129.41835 cm^{-1} . Using the selected SO_2 reference data, the O_3 line center occurs at 1129.4260 \pm .0003 cm^{-1} . The absorption coefficient $k(\nu)$ for all pressures were derived in QUICK and a typical example is shown in figure 12 for the same experimental conditions as in figure 11.

ANALYSIS

The line shape factors are derived by fitting a Voigt function to the absorption coefficient as described above. An example of the best (lowest reduced chi squared) fit for

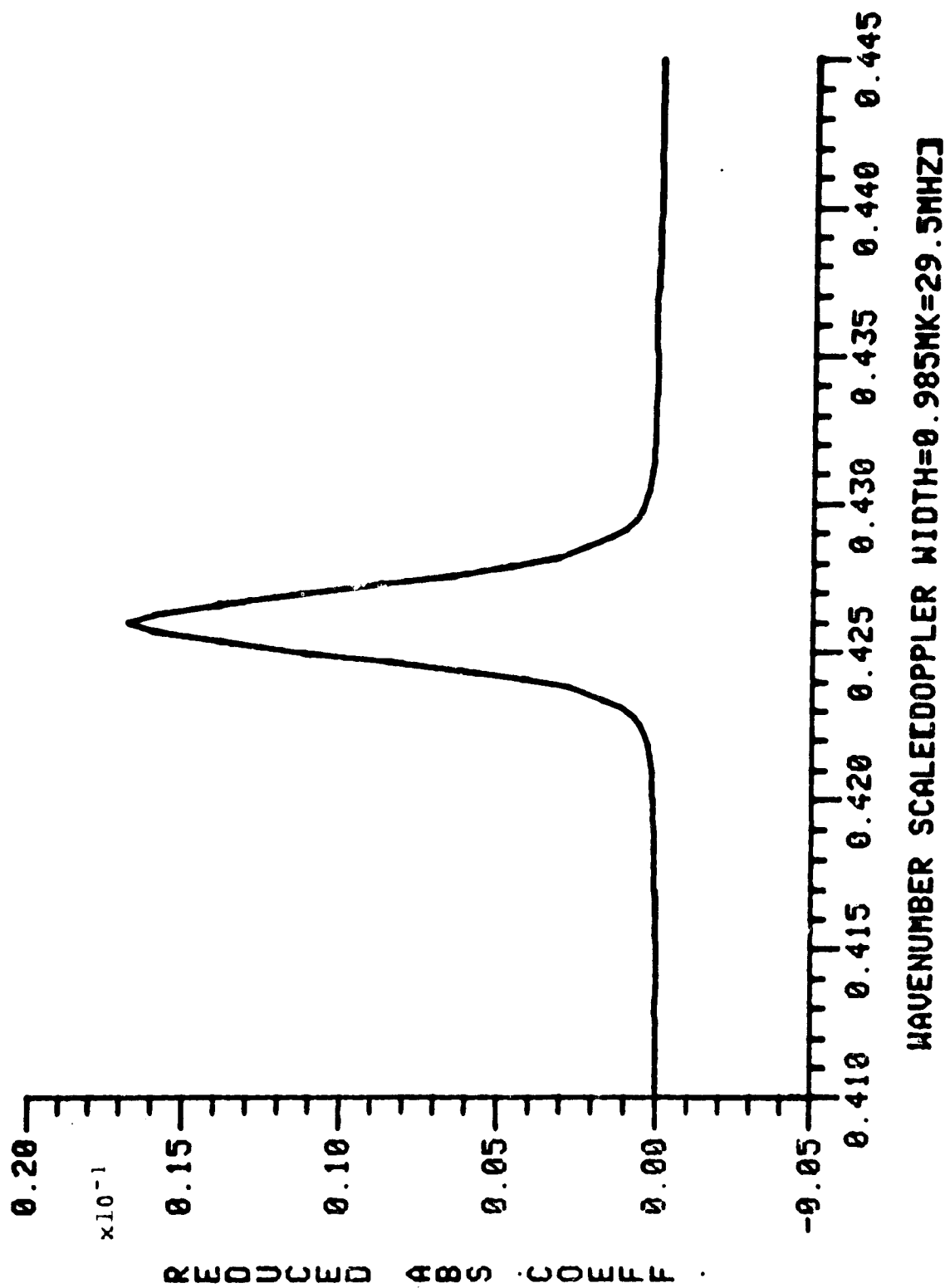


Figure 12. Calculated absorption coefficients at 2.03 Torr and 285K as output by program QUICK.

the same experimental conditions as in figure 11 are shown as figure 13. The Doppler width (HWHM) at 285 K is calculated to be 29.54 MHz. This value was used as the fixed Gaussian portion in the Voigt profile from which the Lorentzian (HWHM) contributions (α_L) were determined as a function of pressure. These are tabulated in Table 2 along with the integrated line strengths. The singular behavior of the 1.49 Torr data warranted its elimination in the final analysis.

A linear least squares fit of the halfwidth data as a function of O_3 pressure shown in figure 14 yields a zero pressure intercept of 15.27 ± 0.29 MHz and a slope (α_0) of 5.71 ± 0.29 MHz/Torr ($\rho=0.99$). This results in a calculated (FWHM) line width at 760 Torr and 296 K of 0.1445 ± 0.007 cm⁻¹ including the Doppler contribution. The zero pressure intercept value cannot be interpreted as the natural line width, since it implies an upper state lifetime of 5.2 nanoseconds, i.e. too fast. Instead this Lorentzian contribution is interpreted as the convolution of the upper and lower state widths, the laser's width (estimated to be 5-10 MHz) and, possibly, a small contribution from power broadening.

The integrated line strengths (Table 2) are found to be independent of pressure and equal to $0.144 \pm 0.007 \times 10^{-20}$ cm⁻¹/molecule-cm⁻² at 285 K.

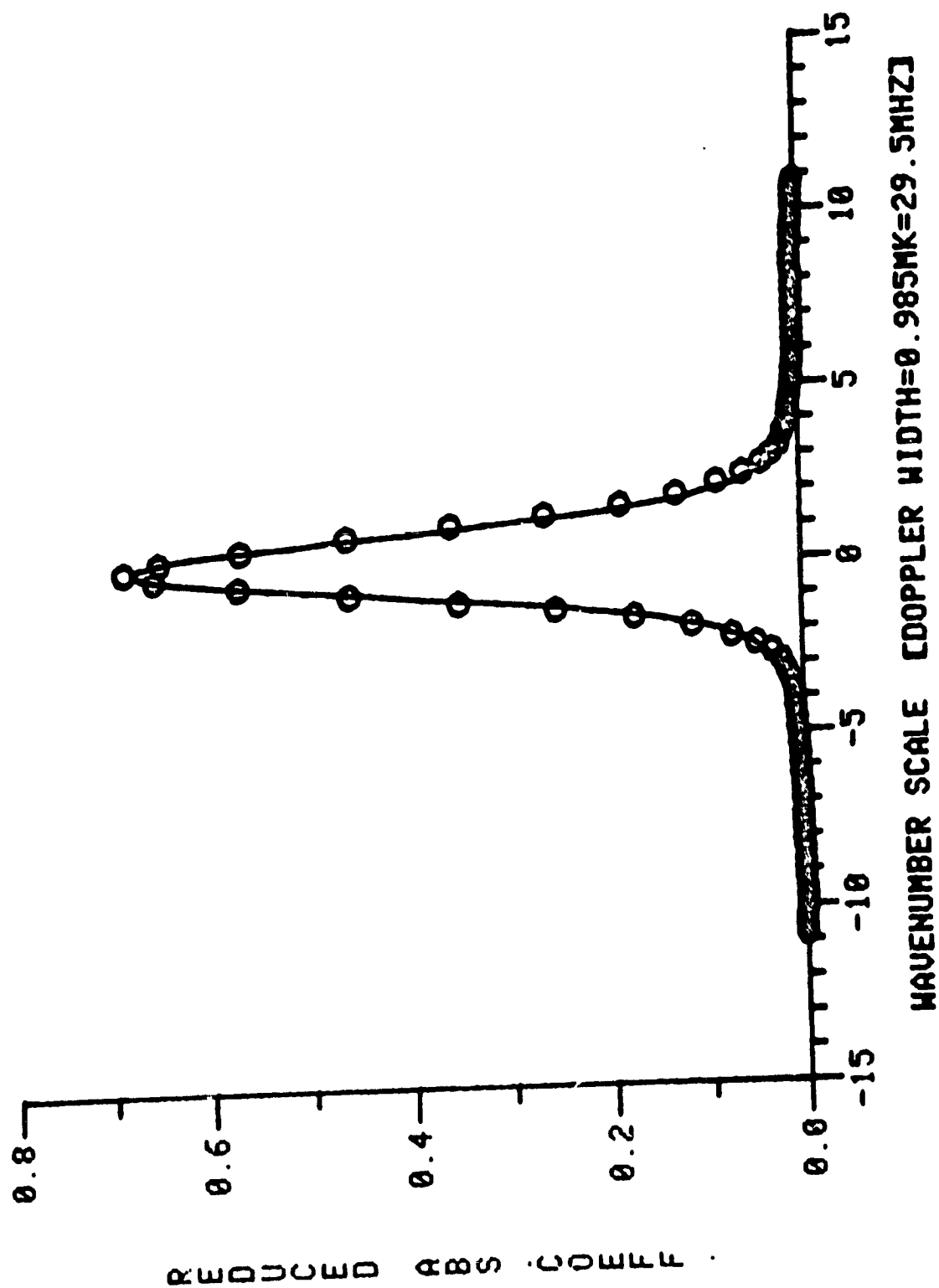


Figure 13. Absorption coefficient profile with best fit Voigt function at 2.03 Torr as determined in program VFIT.

TABLE 2

HALF WIDTHS HWHM AND STRENGTHS VS PRESSURE AT 285 K

Pressure (Torr)	Half Widths		Strengths	
	(mKayser)	(MHz)	(cm ⁻² Torr-l)	Units
0.26	.2942	8.819	.5457	1.542
0.50	.3012	9.060	.5345	1.510
1.00	.3485	10.45	.5198	1.469
2.03	.4616	13.84	.5167	1.460
2.47	.4384	13.14	.4888	1.381
3.01	.5467	16.39	.5126	1.448
3.90	.6167	18.49	.4674	1.321
4.98	.7728	23.17	.4906	1.386
6.29	.8366	25.08	.4978	1.406

 Units = (cm-l/molecule cm-2) x10⁻²¹

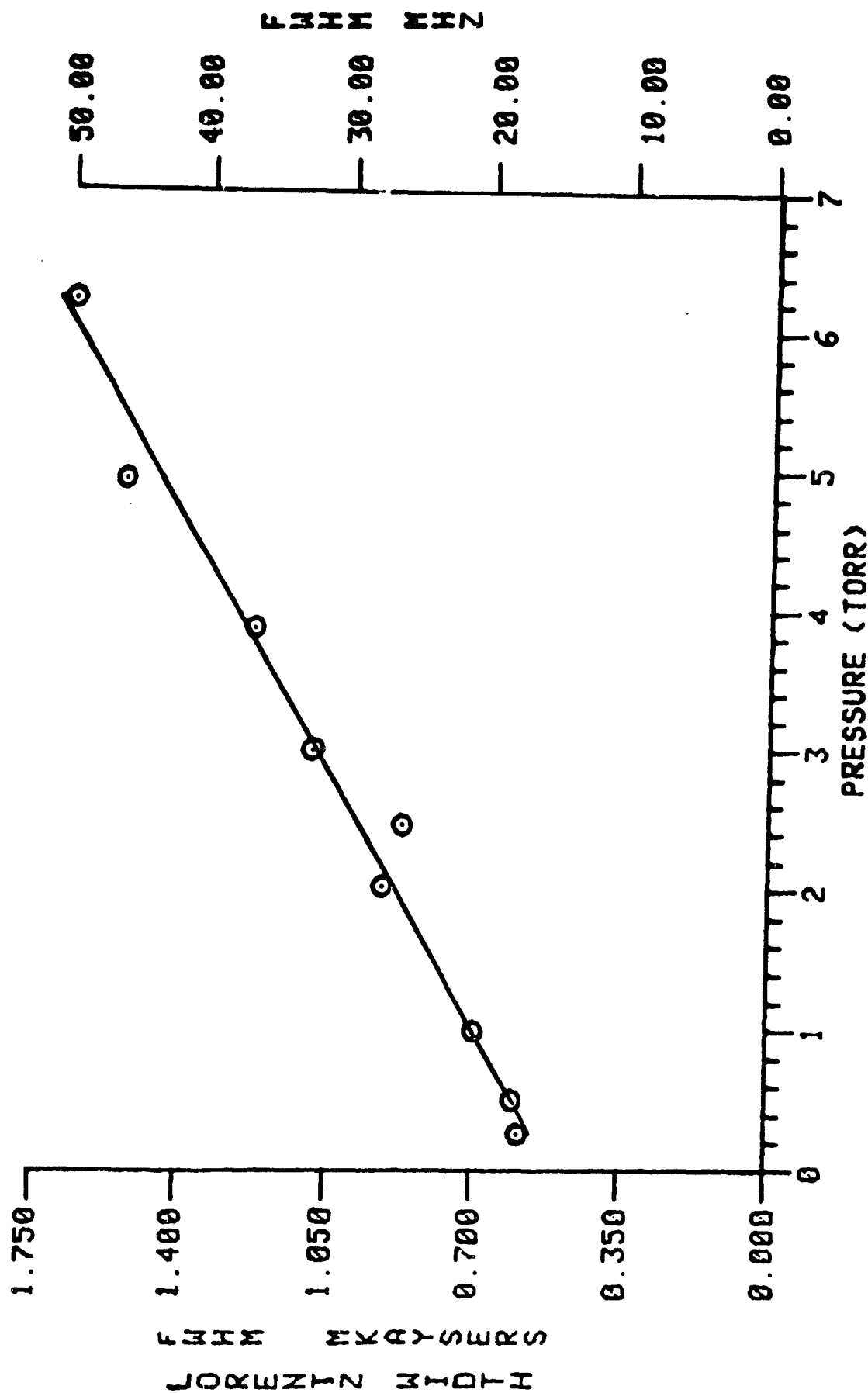


Figure 14. Lorentz FWHM contribution as determined by Voigt fit versus pressure. $Y = .1905 X + .5086$ (mk).

The observed values of $K(0,y)$ as a function of the parameter y (see equation 31) are plotted in figure 15 together with the calculated values. Generally, there is good agreement with the expected broadening function. At the lowest pressures the observed values are somewhat lower than expected, this may be due to the spectral characteristics of the diode laser. Notice here that the value of the ratio α_L/α_D is approximately one, indicating the range of data to be comfortably within the Voigt region.

The Voigt function $K(x,y)$, evaluated at line center, ($X=0$), should be inversely proportional with pressure, see equation 26. Indeed this is the case and is shown in figure 16. A linear least squares fit yields:
 $K(0,y) = 0.7697 - 0.0351 * P(\text{torr})$ with $\rho = -0.977$.

Ozone - ozone collision cross section for this transition and these conditions is calculated utilizing equations (23), (24), and (25) with our halfwidth value of 4.32 GHz (.144 cm-atm-1) and a number density, N , at atmospheric pressure of $2.6 \times 10^{19}/\text{cm}^3 \text{ atm}$. The resulting value of the cross section, σ , is $1.66 \times 10^{15} \text{ cm}^2$.

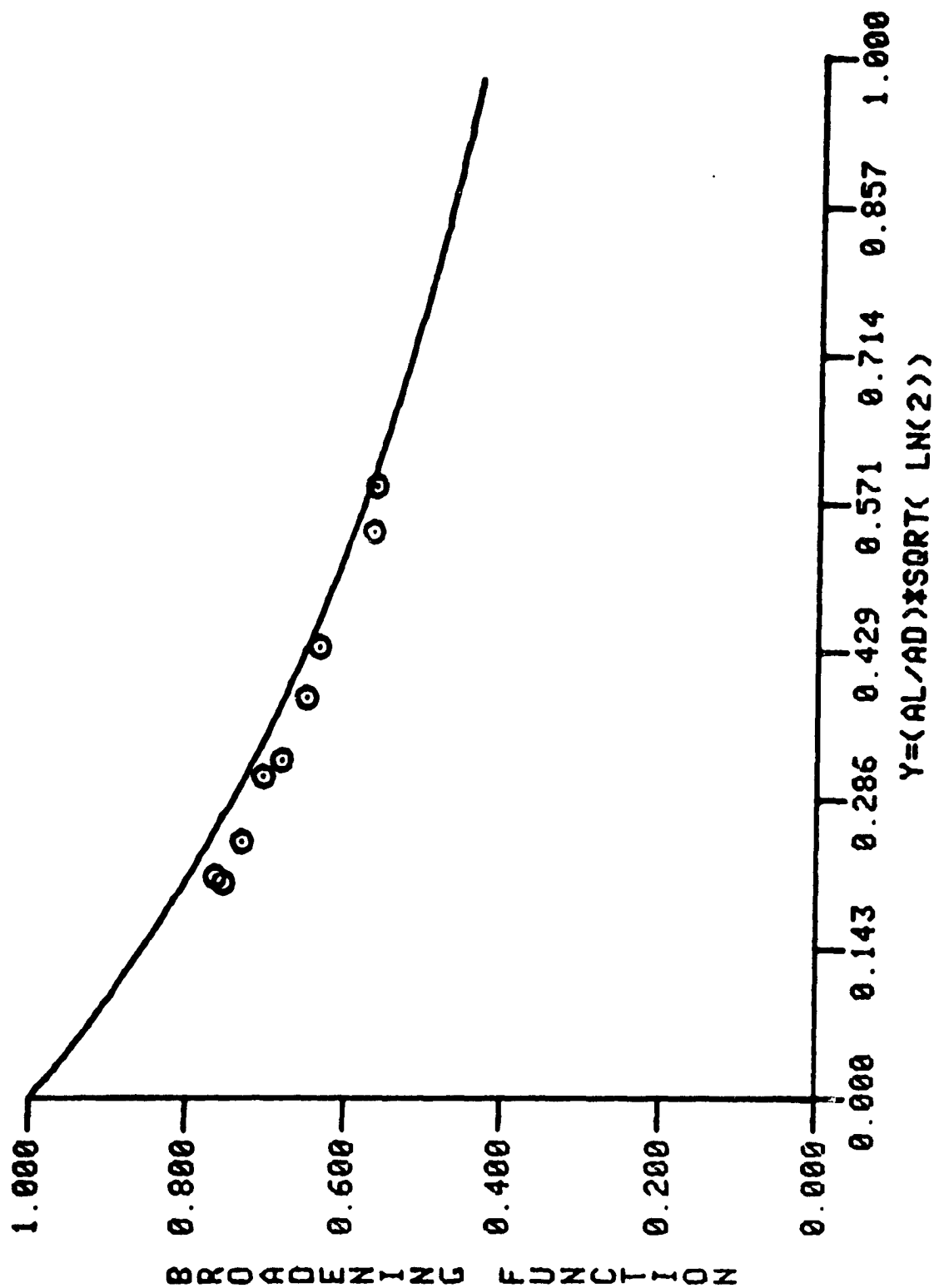


Figure 15. The Voigt reduced absorption coefficient (solid line) and the observed values (circles) plotted as a function of the ratio of Lorentz to Doppler halfwidths (y).

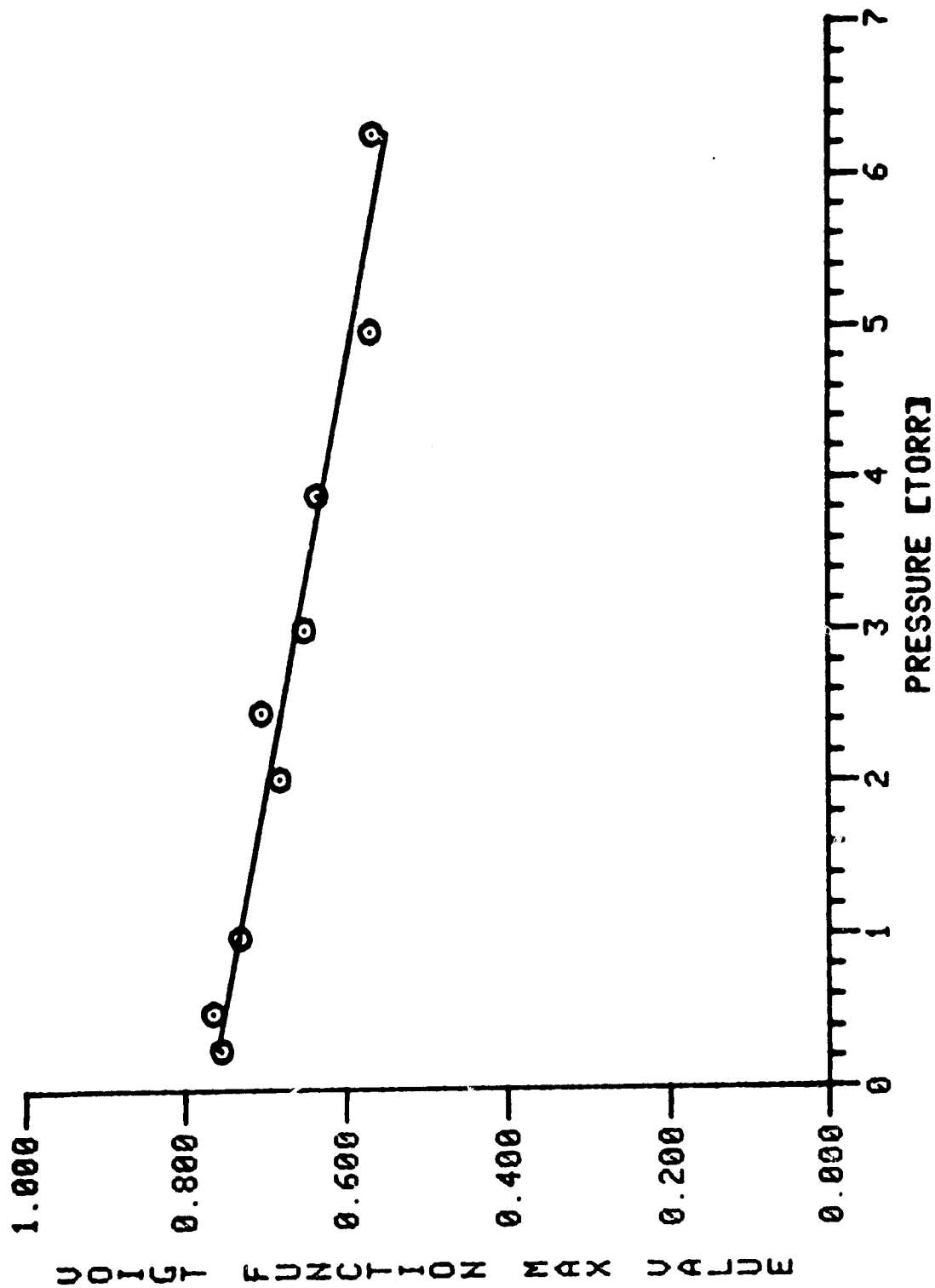


Figure 16. Observed values of the Voigt reduced absorption coefficient, $K(x,y)$ evaluated at line center ($x = 0$) versus ozone pressure.

SUMMARY AND COMPARISONS

The line parameters derived in this experiment are summarized in Table 3 along with the limited work of others.

This short list of available comparisons reveals slight discrepancies especially in the broadening parameter, a_0 , but generally there is reasonable overall agreement.

Line center, ν_0 , is in slight disagreement with the value of 1129.442 cm^{-1} listed on the AFCRL Line Parameters Compilation (1979). The compilation, however, has recently been revised to our value to appear on the 1980 version [38].

CONCLUSIONS

The independent values for self broadened halfwidth and line strength, summarized in table two, have been determined for the 1129.426 cm^{-1} absorption line of ozone in a direct absorption experiment. With this information physical constants may be determined. A workable scheme has been outlined for collection of spectroscopic data as well as software for data reduction and interpretation have been presented.

TABLE 3
COMPARISON OF EXPERIMENTALLY DETERMINED LINE PARAMETERS

Investigator	ν_0 (cm-1)	a (cm-atm)-1	a_0 (MHz/Torr)	S Units
Majorana	1129.426	.144	5.71	.144
Lichtenstein [29]	-	.117	4.63	-
Monnanteuil [35]	-	.124	-	-
AFCRL Tape [32]	1129.426	.110	-	.167

Units = (cm-1/molecule cm-2) $\times 10^{-20}$				

The results are in reasonable agreement with previous investigators microwave data and theoretical calculations in the development of Armstrong, but there is a lack of existing infrared data available for comparison.

This ultra-high resolution measurement will reduce uncertainty in interpretations of retrieved ozone data when applied in remote sensing applications discussed, if used.

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APPENDIX A

PROGRAM QUICK

This program is designed to perform the main data processing tasks as described in detail in the section DATA ANALYSIS. This program is written in Fortran-10 and runs on a DecSystem-10 time shared computer under the Tops10 operating system. Extensive use is made of the Tektronix PLOT10 graphics package, as well as, data handling routines selected from those of Bevington [4] and the International Mathematics and Statistical Library Version 8.0.

```

PROGRAM QUICK
      ANALYSIS PROGRAM FOR SPECTRAL ABSORPTION DATA
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      DIMENSION CUR(501),EMPTY(501),GAS(501),ETALON(501)
      1,ZERO(600),IMAX(4),CSI(3,2),CENTER(2,501),DDS(501)
      2,ETCUR(501)
      COMMON/A/CUR,EMPTY,GAS,ETALON,ZERO
      COMMON/B/CSI,ETCUR,IMAX,CENTER
      DOUBLE PRECISION FILEN

      C
      C      INPUT THE NAME OF THE DATA FILE
      C
      C      TYPE 44
      43      FORMAT(/,1X,' INPUT THE NAME OF THE DATA FILE?',$)
      44      ACCEPT 45,FILEN
      45      FORMAT(A10)
      C
      C
      OPEN(UNIT=21,ACCESS='SEQIN',FILE=FILEN)
      5      CALL DATAIN(N,KK,K2,K3,K4,K10,P3)
      C
      C      ALL ARGUMENTS ARE CHANGED IN SUBROUTINE
      C
      C      USE CURFIT TO CHOP AND ALIGN DATA FOR EACH SCAN.
      GOTO( 10,20,30,40),KK
      10      CONTINUE

```

```

C      I=1
CASE WHERE WE CALL EMPTY
      CALL CURFIT(KK,N,CUR,EMPTY,IMAX,CSI,SIGMA,STORE,L)
      GOTO 5
20     CONTINUE
CASE WHERE I=2 GAS
      CALL CURFIT(KK,N,CUR,GAS,IMAX,CSI,SIGMA,STORE,L)
      IF(K10.EQ. 3) GOTO 55
      GOTO 5
30     CONTINUE
CASE I=3 ETALON
      CALL CURFIT(KK,N,CUR,ETALON,IMAX,CSI,SIGMA,STORE,L)
      GOTO 5
40     CONTINUE
CASE I=4 ZERO (NO CURFIT)
      IMAX(4)=N
50     CONTINUE
CALL ZEROUT(EMPTY,GAS,ETALON,ZERO,IMAX)
c      move above line over to do the plot
CPAUSE
55     CALL NORMAL(EMPTY,GAS,ETALON,IMAX)
C      THE FOLLOWING SUBROUTINE DIFFERENTIATES THE GAS CURVE
C      AND FINDS THE ABSORPTION LINE CENTERS.
      CALL CNTFND(CUR,GAS,IMAX(2),DDS,IPTS,1)
      IF(K10.EQ.3) GO TO 60
C      K10 = 0 IS NOTHING
C      K10 = 1 IS SO2
C      K10 = 2 IS FREON
C      K10 = 3 IS OZONE
      TYPE 433
433    FORMAT(1X,'WOULD YOU LIKE A PLOT OF NORMALIZED
RAW DATA? '$)
      ACCEPT 431,TOPLT
431    FORMAT(A5)
      IF (TOPLT.EQ.'NO') GO TO 434
      CALL NPLOT(DDS,GAS,ETALON,IMAX,IPTS)
434    NT=0
      CALL ABFREQ(DAVE,NT,IPTS,ABCAL,IABS)
      CALL ETPREP(ETALON,DAVE,DDS)
437    CALL ABFREQ(DAVE,NT,IPTS,ABCAL,IABS)
C      NOW READ IN OZONE DATA
      IF(K10.EQ.0) CLOSE(UNIT=21)
      IF(K10.EQ.0) GO TO 43
60     CALL EPLOT(GAS,IPTS,2)
      CALL TAU(P3,IPTS,K2,K3,K4)
      CALL TRANS(P3,IPTS,K2,K3,K4)
      TYPE 69
69     FORMAT(1X,'IS THERE ANOTHER GAS CURVE?',$)
      ACCEPT 79,ANS
79     FORMAT(A5)
      IF(ANS.EQ.'YES') GO TO 43

```



```

CLOSE(UNIT=21)
STOP
END
-----
SUBROUTINE DATAIN(N, KK, K2, K3, K4, K10, P3)

    DIMENSION
    CUR(501), EMPTY(501), GAS(501), ETALON(501), ZERO(600)
    1, ZCUR(600)
    COMMON/A/CUR, EMPTY, GAS, ETALON, ZERO
C READ AND TYPE HEADER DATA
C
10      READ(21, 211) KK, N, K2, K3, K4, K10, TAPENO, P3
211     FORMAT(1X, I2, 1X, I4, 1X, 3(12, 1X), I1, 1X, A5, 1X, F)
C10
READ(21, *) KK, N, K2, K3, K4, K5, K6, K7, K8, K9, K10, K11, TAPENO
C      1, PRES, TOTAV, P3
      IF(K10.EQ.3) GO TO 599
      IF(KK.GT.1) GO TO 910
599     TYPE 900
900     FORMAT(/, 2X, 'READING IN DATA: ', //, 13X, 'KK', 5X,
1       ' OF DATA PTS', 7X, 'DATE', /)
910     TYPE 100, KK, N, K2, K3, K4
      IF( N .GT. 501) TYPE 998
      IF( N .GT. 501) STOP
998     FORMAT(' SORRY CHARLIE----TOO MANY DATA
POINTS!')
C THE HEADER DATA IS AS FOLLOWS:
C
C   KK = TYPE OF SCAN;   KK=1 IS AN EMPTY CELL
C                       KK=2 GAS IN CELL
C                       KK=3 ETALON SCAN
C                       KK=4 OPTICAL ZERO
C                       KK=5 USED TO INDICATE END OF PDP
TAPE
C   N = TOTAL NUMBER OF POINTS
C   K2 = MONTH
C   K3 = DAY
C   K4 = YEAR
C   K5 = RUN
C   K6 = ESTIMATED FREON PRESSURE IN MICRONS...EXCEPT...FOR
C       PDP TAPES 69667, RTT20, 12119, 11800, AND 222 FOR WHICH
C       IT IS GIVEN IN TORR.
C   K7 = ESTIMATED FREQUENCY (IN MORE OR LESS ARBITRARY
UNITS)
C   K8 = STARTING CURRENT
C   K9 = DIODE TEMPERATURE
C   K10 = 1 FOR SO2 (REF GAS), 2 FOR FREON, 3 FOR OZONE
C   K11 = ESTIMATED CELL TEMPERATURE FOR ALL PDP TAPES BEFORE
69667
C       = THERMOCOUPLE READING FOR ALL PDP TAPES AFTER 69667

```

```

(INC)
C  TAPENO = PDP-8 TAPE NUMBER
C  PRES = ESTIMATED TOTAL PRESSURE
C  TOTAV = TEMPERATURE AVERAGED OVER 5 CHANNELS
C  P3 = TOTAL PRESSURE (TORR)
C
      TYPE *,N
      GO TO(20,30,40,50,60),KK
C20  READ(21,*)( (CUR(J),EMPTY(J),J=1,I+4),I=1,N,5)
C
C
20    CALL READDT(CUR,EMPTY,N)
C    DO 25 J=1,N
C25  TYPE 90, CUR(J),EMPTY(J)
      GO TO 60
C30  READ(21,*)((CUR(J),GAS(J),J=1,I+4),I=1,N,5)
C
C
30    CALL READDT(CUR,GAS,N)
C
      GO TO 60
C40  READ(21,*)( (CUR(J),ETALON(J),J=1,I+4),I=1,N,5)
C
C
40    CALL READDT(CUR,ETALON,N)
C
      GO TO 60

C  READ NO MORE THAN 600 ZERO DATA POINTS.
50    IF(KK.EQ.4.AND.N.GT.600) N=600
C51  READ(21,*)( (ZCUR(J),ZERO(J),J=1,I+4),I=1,N,5)
C
C
51    CALL READDT(ZCUR,ZERO,N)
60    CONTINUE
90    FORMAT(F,F)
100   FORMAT(10X,I5,8X,I5,7X,3I4)
110   FORMAT(1X,'THE DATA HAS BEEN READ IN')
C999  FORMAT(10(1X,F7.4))
999   FORMAT(10(F/.4,1X))
C
CHANGED ON JULY 11 FORM 999 FORMAT(10F8.0) TO READ THE
C    DIGITAL TABLET RESULTS
C
C
      RETURN
      END
C-----
      SUBROUTINE CURFIT(KK,N,Y,X,IMAX,C,SIGMA,STORE,L)
      DIMENSION B(2),IMAX(3),SIGMA(3),X(1),Y(1),C(3,2)
CHOPS AND  ALIGNS THE DATA

```

```

        IF(KK .NE. 1)      GO TO 110
C   SMOOTH EMPTY CELL DATA ONLY
    50      CALL SMOOTH(X,N)
        XMAX=X(1)
C   FIND THE ACTUAL MAXIMUM DETECTOR SIGNAL, X(KMEAN)
        DO 60 I=2,N
        IF(X(I) .LT. XMAX)      GO TO 60
        XMAX=X(I) ; KMEAN=I
    60      CONTINUE
CUTOFF IS THE DETECTOR LEVEL BELOW WHICH THE LOWER 10%
C   IS DREGARDED TO ELIMINATE THE PORTIONS OF DATA
C   WITH LOW S/N RATIO.
        CUTOFF=0.1*XMAX
C   FIND THE FIRST POINT ABOVE CUTOFF (KMIN).
        KMIN=1
        DO 70 I=1,N
        IF(X(I) .LT. CUTOFF)      GO TO 70
        KMIN=I ; GO TO 80
    70      CONTINUE
    80      CONTINUE
C   FIND THE LAST POINT ABOVE CUTOFF (KMAX).
        KMAX=N
        DO 90 I=1,N
        K=N+1-I
        IF(X(K) .LT. CUTOFF)      GO TO 90
        KMAX=K ; GO TO 100
    90      CONTINUE
    100     CONTINUE
CHECK THAT KMEAN IS NOT AT THE END OF THE CURRENT SCAN
C   (WITHIN 2 POINTS OF END). IF IT IS, SET IT IN THE
MIDDLE.
        IF(KMEAN .GT. (N-2))      KMEAN=(KMAX+KMIN)/2
C   SMOOTH CURVES FOR ETALON AND GAS DATA
    110     CONTINUE
        IF(KK .EQ. 3)      CALL SMOOTH(X,N)
        IF(KK .EQ. 2)      CALL SMOOTH(X,N)
C   DEFINE KT2, THE NUMBER OF POINTS BETWEEN KMIN and KMAX +
1.
        KT2=KMAX-KMIN+1
        XKMIN=X(KMIN)
        CALL LINFIT(XKMIN,Y(KMIN),KT2,B,SIGMA(KK),2)
C   STORE SLOPE AND INTERCEPT OF CURRENT VS LOCATION IN
C   ARRAY CALCULATED IN LINFIT.
        DO 190 I=1,2
        C(KK,1) = INTERCEPT
        C(KK,2) =SLOPE
    190      C(KK,I)=B(I)
COUNT (KOUNT) THE NUMBER OF POINTS GREATER THAN 3SIGMA AWAY
FROM
C   THE CALCULATED STRAIGHT LINE. (HOPEFULLY THERE ARE
NONE)

```

```

C   PRINT THIS VALUE AT END OF ROUTINE.
      SIG3=3.0*SIGMA(KK)
      KOUNT=0
      DO 200 I=1,N
      AMP=C(KK,1)+C(KK,2)*I
      DIF=ABS(AMP-Y(I))
      IF(DIF .GT. SIG3)      KOUNT=KOUNT+1
200   CONTINUE
CALCULATE WHAT THE CURRENT IS FROM THE STRAIGHT LINE FIT
C   (EMPTY CELL ONLY)
      IF(KK .GT. 1)      GO TO 210
C   Y = MX + B
C   CURRENT = SLOPE X ORDINATE + INTERCEPT
      YMIN = C(KK,2)*KMIN + C(KK,1)
      YMEAN = C(KK,2)*KMEAN + C(KK,1)
      YMAX = C(KK,2)*KMAX + C(KK,1)
210   CONTINUE
C   RECALCULATE KMIN and KMAX FOR ALL SCANS FROM
C   SLOPE AND INTERCEPT STRAIGHT LINE FIT FOUND IN LINFIT.
C   X = Y - B / M = KMIN
      KMIN=(YMIN-C(KK,1))/C(KK,2)
      KMAX=(YMAX-C(KK,1))/C(KK,2)
CHECK THAT KMIN IS NOT ZERO
      IF(KMIN .LE. 0)      KMIN=1
CHECK KMAX IS AT LEAST 2 POINTS FROM THE END DATA POINT IF
IT
C   HAPPENS TO APPEAR THERE
      IF(KMAX .GT. (N-2))KMAX=N-2
      KMEAN=(YMEAN-C(KK,1))/C(KK,2)
C   SHIFT AND ALIGN THE ARRAYS!
      K=0
      DO 220 I=KMIN,KMAX
      K=K+1
      IF(I.EQ.KMEAN)      STORE=K+.5
220   X(K)=X(I)
      IMAX(KK)=K
C   IMAX IS THE ARRAY POSITION OF THE MAX CURRENT USED.
C   TYPE 230, KK, N, K, KMIN, KMAX, KOUNT, STORE,
C   1 C(KK,1), C(KK,2), SIGMA(KK)
      RETURN
230   FORMAT(6I5, F7.1, 1PE12.3, 2E12.3)
      END
C-----
C   SUBROUTINE SMOOTH
C
C   PURPOSE:
C   SMOOTH A SET OF DATA POINTS BY AVERAGING ADJACENT
C   CHANNELS
C
C   USAGE:
C   CALL SMOOTH(Y, NPTS)

```

```

C
C      DESCRIPTION OF PARAMETERS:
C      Y-ARRAY OF DATA POINTS
C      NPTS-NUMBER OF DATA POINTS
C      SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED:
C      NONE

```

```

C      SUBROUTINE SMOOTH(Y,NPTS)
      DIMENSION Y(1)
11      IMAX=NPTS-1
      YI=Y(1)
21      DO 24 I=1,IMAX
      YNEW=(YI+2.*Y(I)+Y(I+1))/4.
      YI=Y(I)
24      Y(I)=YNEW
25      Y(NPTS)=(YI+3.*Y(NPTS))/4.
      RETURN
      END

```

C-----

```

      SUBROUTINE LINFIT(XI,Y,N,B,SIGMA,NTIMES)
      DIMENSION Y(1),B(2)
C      THIS ROUTINE CHECKS THAT THE CURRENT IS RECORDED
C      AT A CONSTANT RATE; THAT IS, CHECKS CURRENT VS TIME
C      OR POSITION IN ARRAY, BY A LEAST SQUARES FIT.
C      GIVES THE SLOPE AND INTERCEPT AS OUTPUT RESULTS (B).
      SIGMA=1.0E+08
10      M=0
      SX=0.0;SY=0.0;SXX=0.0;SXY=0.0
      DO 30 I=1,N
      IF(SIGMA .GT. 1.0E+07)      GO TO 20
      F=B(1)+B(2)*(XI-1+I)
      DIF=ABS(F-Y(I))
      IF(DIF .GT. SIG3)      GO TO 30
20      X=XI-1+I
      SX=SX+X
      SY=SY+Y(I)
      SXX=SXX+X*X
      SXY=SXY+X*Y(I)
      M=M+1
30      CONTINUE
      B(2)=(M*SXY-SX*SY)/(M*SXX-SX*SX)
      B(1)=(SY-B(2)*SX)/M
      SUM=0.0
      IF(SIGMA .GT. 1.0E+07)      GO TO 50
      DO 40 I=1,M
      F=B1+B2*(XI-1+I)
      DIF=ABS(F-Y(I))
      IF(DIF .GT. SIG3)      GO TO 40
      F=B(1)+B(2)*(XI-1+I)
      SUM=SUM+(F-Y(I))*(F-Y(I))

```

```

40      CONTINUE
      SIGMA=SQRT(SUM/M)
      ICOUNT=N-M
      GO TO 70
50      DO 60 I=1,N
      F=B(1)+B(2)*(XI-1+I)
60      SUM=SUM+(F-Y(I))*(F-Y(I))
      SIGMA=SQRT(SUM/N)
      SIG3=3.0*SIGMA
      B1=B(1) ; B2=B(2)
      IF(SIGMA .GT. 1.0E+07) SIGMA=1.0E+06
      IF(NTIMES .EQ. 1) GO TO 70
      GO TO 10
70      RETUPN
      END

```

C-----

```

      SUBROUTINE NORMAL(EMPTY,GAS,ETALON,IMAX)
C  PURPOSE:
C  TO NORMALIZE GAS AND ETALON DATA
C  FOR PLOTTING NORMALIZED TRANSMITTANCE PLOTS.
      DIMENSION EMPTY(1),GAS(1),ETALON(1),IMAX(1)
      IF(IMAX(2) .NE. IMAX(3) ) TYPE 300
300      FORMAT(' IN NORMAL IMAX(2) .NE. IMAX(3)')
C
CHECK TO SEE IMAX(1)=IMAX(2)=IMAX(3)
C      IF NOT FORCE THEM TO BE EQUAL TO THE SMALLEST OF
THEM
      IM=MINO(IMAX(1),IMAX(2),IMAX(3) )
C
C      FORCE ALL TO BE IM
      IMAX(1)=IM
      IMAX(2)=IM
      IMAX(3)=IM
C
C
C
C
C
      DO 10 I=1,IMAX(2)
10      GAS(I) = GAS(I)/EMPTY(I)
      DO 20 I=1,IMAX(3)
      ETALON(I) = ETALON(I)/EMPTY(I)
20      CONTINUE
C      PAUSE
      RETURN
      END

```

C-----

```

      SUBROUTINE CNTFND(CUR,GAS,NPTS,DDS,IPTS,KT)
      DIMENSION
DS(501),CENTER(2,501),BPAR(4),C(501,3),

```

```

1DDS(501),GAS(1),CUR(1),ETCUR(501),CSI(3,2),IMAX(4)
COMMON/B/CSI,ETCUR,IMAX,CENTER
C  PURPOSE: TO FIND LINE CENTERS OF GAS DATA
C  PASSED TO ROUTINE:
C  DS = ARRAY OF POINTS 1ST DERIVATIVE SPECTRUM
C  NPTS = LENGHT OF THE ARRAY
C  KT = TYPE OF SCAN IDENTIFIER. IF KT=2 THIS ROUTINE
C  WILL FIND CENTER MAXJMUMS. KT=ANYTHING ELSE IT
C  FINDS MINIMUMS.
C
C  PASSED BACK TO CALLING PROGRAM:
C
C  CENTER = ARRAY OF LINE POSITIONS OF THE LINE
CENTERS
C          (1,501) = GAS CENTERS DATA
C          (2,501) = ETALON PEAKS DATA
C  IPTS = NUMBER OF LINES = NUMBER OF ENTERIES IN
CENTER
C
C  (REQUIRED FOR SUPRESSION OF 2ND DIFF. CALCULATION)
C  IC=501
C
C  CSAVE THE ORIF NGONAL ARRAY AND USE DDS AS A NEW CURRENT
ARRAY
C
C  TYPE FIRST 10 ENTRIES OF CUR GOING INTO FILL
C  DO 76 I2=1,10
C76      TYPE 78,(I2,CUR(I2))
      CALL FILL(NPTS,CUR,DDS)
C  TYPE FIRST 10 ENTRIES OF NEW ARRAY DDS COMING FROM
FILL
C  DO 77 I1=1,10
C77      TYPE 78 ,(I1,DDS(I1))
78      FORMAT(1X,I4,F)
      DO 601 IK=1,4
601      BPAR(IK)=0.0
C
C  SMOOTH THE DATA 1ST
      NSMOOT=5
      DO 330 IK=1,NSMOOT
330      CALL SMOOTH(GAS,NPTS)
      CALL ICSICU(DDS,GAS,NPTS,BPAR,C,IC,IER)
      CALL DCSEVU(DDS,GAS,NPTS,C,IC,DDS,DS,NPTS,DDS,0,IER)
C  THIS LOOP FINDS WHERE LINE CENTERS OCCUR BY CHECKING
C  WHERE THE FIRST DERIVATIVE( FOUND IN DCSEVU) PASSES
C  THROUGH ZERO FROM +TO -.
      DO 332 IK=1,NSMOOT
332      CALL SMOOTH(DS,NPTS)
      IPTS=0
      DO 60 NPT=1,NPTS-1
      PT1 = DS(NPT)

```

```

        PT2 = DS(NPT+1)
        IF(KT.EQ.2)GO TO 10
C      MIN FINDING LOOP
C      DETERMINES WHERE THE DIFFERENTIATED ARRAY (DS)
C      PASSES THROUGH ZERO FROM + TO -.
        IF(PT1-PT2)40,40,60
40      IF(PT1.LT.0.0 .AND.PT2.GT.0.0) GOTO 50
        GO TO 60
C      MAX FINDING LOOP
C      DETERMINES WHERE THE DIFFERENTIATED ARRAY (DS)
C      PASSES THROUGH ZERO FROM + TO -.
10      CONTINUE
        IF(PT1-PT2)60,45,45
45      IF(PT1.GT.0.0.AND.PT2.LT.0.0) GO TO 50
        GOTO 60
CHECK THE 2ND DERIVATIVE TO SEE IF <0.0 THEN A MINIMUM FOR
SURE
C50      IF( DDS(NPT+1) .GE. 0.0) GOTO 60
50      CONTINUE
C
        IPTS=IPTS+1
C      INTEPOLATE
C
CENTER(KT,IPTS)=DDS(NPT)-(PT1/(PT2-PT1))*(DDS(NPT+1)-DDS(NPT))
C
CENTER(KT,IPTS)=CUR(NPT)-(PT1/(PT2-PT1))*(CUR(NPT+1)-CUR(NPT))

60      CONTINUE
        TYPE 62,IPTS,CENTER(KT,IPTS)
62      FORMAT(1X,' ',I4,' CENTERS LAST LINE IS ',F,/)
        IF( IPTS .EQ. 0) TYPE 8883
8883     FORMAT(' NO LINE CENTERS FOUND-----CONTINUUM')
        RETURN
        END
C-----
        SUBROUTINE NPLOT(CUR,GAS,ETALON,IMAX,IPTS)
        DIMENSION CUR(1),GAS(1),ETALON(1),IMAX(3),ISTRIN(15)
        1,IVERT(13),CENTER(2,1),IXLAB1(7)
        DATA
ISTRIN/78,79,82,77,65,76,73,90,69,68,32,80,76,79,84/
        DATA IVERT/84,82,65,78,83,77,73,84,84,65,78,67,69/
        DATA IXLAB1/67,85,82,82,69,78,84/
C      PLOTS NORMALIZED DATA
        CALL INITT(120)
        AMIN=1000.
        AMAX=-100000.
        CALL BINITT
        CALL NPTS(IMAX(2))

```



```

      CALL MNMX(GAS,AMIN,AMAX)
      CALL DLIMY(0.,AMAX)
      CALL XFRM(2)
      CALL YFRM(2)
      CALL CHECK(CUR,GAS)
      CALL DSPLAY (CUR,GAS)
      IF( IPTS .GE.1)CALL ARROW(IPTS,1)
CALL ARROW ONLY IF THERE ARE REALLY SEPERATE LINES
      CALL NPTS(IMAX(3))
CALL LINE(2)
      CALL CPLOT(CUR,ETALON)
      CALL MOVABS(650,730)
      CALL HLABEL(15,ISTRIN)
      CALL MOVABS(400,50)
      CALL HLABEL(7,IXLAB1)
      CALL MOVABS(25,500)
      CALL VLABEL(13,IVERT)
      CALL BELL
      CALL TINPUT(ANS)
      RETURN
      END
C-----
      SUBROUTINE ARROW(IPTS,KT)
      DIMENSION CSI(3,2),CENTER(2,501),IMAX(4),ETCUR(501)
      COMMON/B/CSI,ETCUR,IMAX,CENTER
C      PLOT A LINE AT THE POINTS WHERE WE HAVE FOUND A
C      SPECTRAL LINE BY LOOKIG AT THE 1ST DERIVATIVE
C
      CALL NPTS(IPTS)
      YMAX=.10
      YMIN=.05
      DO 10 I=1,IPTS
      CALL MOVEA(CENTER(KT,I),YMAX)
      CALL DRAWA(CENTER(KT,I),YMIN)
10      CONTINUE
      RETURN
      END
C-----
C
      SUBROUTINE FILL(NPTS,X,XNEW)
C
      DIMENSION X(1),XNEW(1)
C
      PURPOSE: TAKE AN ARRAY (X) THAT HAS REPEATING
SEQUENCES
C      OF NUMBERS AND CHANGE IT SUCH THAT IT IS
MONOTONICALLY
C      ASCENDING IN VALUE
C

```

```

C      RETURNED ARRAY IS XNEW
C
C      SAVE THE OLD ARRAY
C
      DO 300 I=1,NPTS
300      XNEW(I)=X(I)
      FS=XNEW(1)
      NSAME=0
      DO 20 I=2,NPTS
      IF( XNEW(I)-FS) 8,7,10
7      NSAME=NSAME+1
      IF( I .EQ. NPTS) GOTO 14
      GOTO 20
10      FS=XNEW(I)
      IF( NSAME .GT.1 .AND. I .LT. NPTS) GOTO 11
      IF( NSAME .EQ.0) GOTO 20
C
C      JUST 2 NUMBERS ARE THE SAME
      XNEWCH=XNEW(I)-XNEW(I-1)
      XNEW(I-1)=XNEW(I-1)+XNEWCH/2.
      NSAME=0
      GOTO 20
11      CONTINUE
      NT=0
      DO 13 J=I-NSAME,I-1
      NT=NT+1
XNEW(J)=XNEW(J)+NT*(XNEW(I)-XNEW(I-NSAME-1))/FLOAT(NSAME+1)
13      CONTINUE
      NSAME=0
      GOTO 20
8      WRITE(5,100)
100     FORMAT('      ARRAY IS DECREASING IN
VALUE*****')
20      CONTINUE
      RETURN
C
C      MAKE SURE LAST ONE IS DIFFERENT THAN NEXT TO LAST
ONE
14      NT=0
      DO 16 J=NPTS-NSAME+1,NPTS
      NT=NT+1
16      XNEW(J)=XNEW(NPTS-NSAME)+NT*(
XNEW(NPTS)-XNEW(1))/FLOAT(NPTS)
      RETURN
      END
C-----
      SUBROUTINE ETPREP(ETALON,DAVE,DDS)
      DIMENSION
      DDS(1),CENTER(2,501),D(100),FREQ(100),WTH(100)

```

```

1,CSI(3,2),ETCUR(501),ETALON(1),IMAX(4)
COMMON/B/CSI,ETCUR,IMAX,CENTER
C      THIS ROUTINE CONSIDERS THE ETALON TRACE
ALONE, PREPARING
C      IT FOR LATER CONVERSION TO RELATIVE AND ABSOLUTE
C      FREQUENCY. ETALON PEAKS AND THE CHANGE OF CURRENT
BETWEEN
C      THEM IS FOUND THEN A SHORT STATISTICAL ANALYSIS IS
C      PERFORMED. A HISTOGRAM PLOT IS OUTPUT, USEFUL TO
C      DETERMINE MODE SHIFTS.
C      RECALCULATE ETALON CURRENT ARRAY FROM SLOPE and
INTERCEPT.
      NPTS = IMAX(3)
      DO 5 NE=1,NPTS
5      ETCUR(NE) = ((CSI(3,2))*FLOAT(NE))+CSI(3,1)
C      DO 73 I=1,10
C      TYPE 6,I,ETCUR(I)
73      CONTINUE
C      SHIFT ARRAYS IF NECESSARY, SO CURRENT BEGINS AT ZERO.
      IF(ETCUR(1).LT.0.0)GO TO 41
      GO TO 51
41      SHIFT = ETCUR(1)
      DO 51 I=1,NPTS
      ETCUR(I) = ETCUR(I)-SHIFT
51      CONTINUE
C      DO 7 I=1,10
C      TYPE 6,I,ETCUR(I)
6      FORMAT(1X,'ETCUR(',I2,') = ',F)
7      CONTINUE
C      SMOOTH THE DATA
      NSMOOT = 10
      DO 330 IK=1,NSMOOT
330      CALL SMOOTH(ETALON,NPTS)
C      DO 9 I=1,10
C      TYPE 8,I,ETALON(I)
8      FORMAT(1X,'ETALON(',I2,') = ',F)
9      CONTINUE
C      FIND CENTERS OF ETALON PEAKS.
      CALL CNTFND(ETCUR,ETALON,NPTS,DDS,IEPTS,2)
C      FIND CHANGE OF CURRENT BETWEEN PEAKS, STORE IN
ARRAY D().
      NUM=IEPTS-1
      DO 10 N=1,NUM
      D(N) = CENTER(2,N+1)-CENTER(2,N)
10      CONTINUE
C      FIND AVERAGE CHANGE OF CURRENT BETWEEN PEAKS
(DAVE).
      DTOT = 0.
      DO 20 M=1,NUM
20      DTOT=DTOT+D(M)
      DAVE=DTOT/FLOAT(NUM)

```

```

TYPE 435
435   FORMAT(1X,'WOULD YOU LIKE A SHORT STATISTICAL
PLOT      1 OF THE ETALON TRACE? '$)
ACCEPT 436,STAT
436   FORMAT(A5)
IF (STAT.EQ.'NO') GO TO 437
C     PLOT ETALON TRACE AND CENTERS FOUND
CALL EPLOT(ETALON,IEPTS,1)
DO 14 N=1,NUM
TYPE 15,N,D(N)
15    FORMAT(1X,'D(',I2,') = ',F)
14    CONTINUE
TYPE 25, DAVE
25    FORMAT(1X,'DAVE = ',F)
C     FIND STANDARD DEVIATION, (SIG)
SUM=0.
DO 30 I=1,NUM
SUM=SUM+(D(I)-DAVE)**2
30    CONTINUE
SIG=SQRT(SUM/(FLOAT(NUM)-1.))
TYPE 40, SIG
40    FORMAT(1X,'STANDARD DEVIATION IS',F)
PAUSE
C     AT THIS POINT WIDTHS OF ETALON PEAKS WILL BE
C     COMPARED IN ORDER TO DETECT SUBTLE MODE SHIFTS
C     THAT MAY HAVE BEEN PREVIOUSLY OVERLOOKED. THE
C     WIDTHS WILL BE SORTED AND PLOTTED VS THEIR
C     FREQUENCY OF OCCURANCE, (HISTOGRAM).
C     THE DISTRIBUTION SHOULD BE GAUSSIAN!
C     FIND MIN AND MAX ETALON PEAK WIDTHS,(DMIN and
DMAX).
DMIN=D(1)
DO 50 K=2,NUM
50    IF(D(K).LT.DMIN)DMIN=D(K)
DMAX=D(1)
DO 60 L=2,NUM
60    IF(D(L).GT.DMAX) DMAX=D(L)
C     WHAT IS THE RANGE IN VALUES OF D?
RANGE = DMAX-DMIN
C     BUILD ARRAY OF SLOTS.
XINC = RANGE / FLOAT(NUM-1)
WTH(1)=DMIN
DO 70 N=2,NUM
70    WTH(N) = WTH(N-1)+XINC
C     SORT ETALON WIDTHS AND FIND THEIR FREQUENCY OF
OCCURANCE, FREQ(I).
DO 90 M=1,NUM
I=1
85    IF(D(M).LE.WTH(I)) GO TO 87
I = I+1

```

```

      GO TO 85
87      FREQ(I)=FREQ(I)+1.
90      CONTINUE
C      CALL PLOT ROUTINE TO PLOT HISTOGRAM.
      CALL HISPLT(WTH,FREQ,NUM)
437     RETURN
      END
C-----
      SUBROUTINE HISPLT(WTH,FREQ,NUM)
      DIMENSION FREQ(1),WTH(1),IYLAB(17),IXLAB(12)
      DATA
IYLAB/70,82,69,81,32,79,70,32,79,67,67,85,82,65,78,67,69/
      DATA IXLAB/69,84,65,76,79,78,32,87,73,68,84,72/
      TYPE 10,NUM
10      FORMAT('      FREQ      WIDTH      NUM=',I)
      DO 20 I=1,NUM
20      TYPE 21,(FREQ(I),WTH(I))
21      FORMAT(1X,F,1X,F)
C      PAUSE
C      PLOT THE HISTOGRAM
      CALL INITT(120)
      CALL BINITT
      CALL NPTS(NUM)
      CALL VBA1ST(8,0,0)
      CALL XFRM(1)
      CALL YMFRM(1)
      CALL CHECK(WTH,FREQ)
      CALL DSPLAY(WTH,FREQ)
      CALL MOVABS(400,20)
      CALL HLABEL(12,IXLAB)
      CALL MOVABS(25,575)
      CALL VLABEL(17,IYLAB)
      CALL BELL
      CALL TINPUT(ANS)
      RETURN
      END
C-----
      SUBROUTINE EPLOT(ETALON,IEPTS,ITYFG)
      DIMENSION ETCUR(501),ETALON(1),ISTRIN(15),CSI(3,2)
      1,IVERT(13),CENTER(2,501),IMAX(4)
      DIMENSION IVERT3(15),IETSTR(23)
      DIMENSION IXLAB1(7),IXLAB3(13)
      COMMON/B/CSI,ETCUR,IMAX,CENTER
      DATA
ISTRIN/78,79,82,77,65,76,73,90,69,68,32,80,76,79,84/
      DATA IVERT/84,82,65,78,83,77,73,84,84,65,78,67,69/
      DATA IVERT3/65,66,83,32,67,79,69,70,32,
1 66,65,83,69,32,69/
      DATA IXLAB1/67,85,82,82,69,78,84/
      DATA IXLAB3/65,66,83,32,70,82,69,81,85,69,78,67,89/
      DATA

```

```

IETSTR/69,84,65,76,79,79,32,65,78,68,32,80,69,65,75,
1 32,67,69,78,84,69,82,83/
C   PLOTS NORMALIZED GAS DATA
      IVALUE = IMAX(3)
      CALL INITT(120)
      CALL BINITT
      CALL NPTS(IVALUE)
      CALL XFRM(2)
      CALL YFRM(2)
      CALL CHECK(ETCUR,ETALON)
      CALL DSPLAY (ETCUR,ETALON)
      IF( IEPTS .CL.1)CALL ARROW(IEPTS,2)
CALL ARROW ONLY IF THERE ARE REALLY SEPERATE LINES
      CALL MOVABS(600,730)
      IF(ITYFG.EQ.1)CALL HLABEL(23,IETSTR)
      IF(ITYFG.EQ.1.OR.ITYFG.EQ.3)GO TO 10
      CALL HLABEL(15,ISTRIN)
10      CALL MOVABS(25,500)
      IF(ITYFG.EQ.1.OR.ITYFG.EQ.2)CALL VLABEL(13,IVERT)
      CALL MOVABS(25,600)
      IF(ITYFG .EQ. 3) CALL VLABEL(15,IVERT3)

C
C      NOW PUT IN THE X LABELS
C
      CALL MOVABS(425,25)
      IF(ITYFG.EQ.1) CALL HLABEL(7,IXLAB1)
      IF(ITYFG.EQ.3.OR.ITYFG.EQ.2)CALL HLABEL(13,IXLAB3)

C
C
      CALL BELL
      CALL TINPUT(ANS)
      ITYFG=0
      RETURN
      END

C-----
      SUBROUTINE RLFREQ(DAVE,IPTS)
      DIMENSION CENTER(2,501),ETCUR(501),CSI(3,2),IMAX(4)
      COMMON/B/CSI,ETCUR,IMAX,CENTER
C   THIS ROUTINE CONVERTS THE CURRENT ARRAY TO RELATIVE
FREQUENCY
      NPTS = IMAX(3)
C   THERE ARE .02445 CM-1 BETWEEN PEAKS.
C   FIND A CONVERSION FACTOR (CONF)

      CONF = .02445/DAVE
C   CONVERT CURRENT TO RELATIVE FREQS.
      DO 10 J=1,NPTS
10      ETCUR(J) = ETCUR(J)*CONF
C      DO 30 I=1,1000,10
C      TYPE 20,I,ETCUR(I)
20      FORMAT(1X,'ETCUR(',I2,') = ',F)

```

```

30      CONTINUE
CONVERT GAS CENTER ARRAY TO REL FREQS.
      DO 40 K=1,IPTS
      CENTER(1,K) = (CENTER(1,K))*CONF
40      CONTINUE
      RETURN
      END
C-----
      SUBROUTINE ABFREQ(DAVE,NT,IPTS,ABCAL,IABS)
      DIMENSION CSI(3,2),ETCUR(501),IMAX(4),CENTER(2,501)
      COMMON/B/CSI,ETCUR,IMAX,CENTER
C      ABFREQ CONVERTS THE CURRENT ARRAY FIRST TO RELATIVE
C      FREQUENCIES (CALLING RELFREQ), THEN TO ABSOLUTE
C      FREQS.
C      IT ASKS WHICH LINE OF THE REFERENCE SPECTRUM IS TO
C      BE
C      USED FOR FREQUENCY CALIBRATION AND ITS KNOWN CENTER
C      FREQ.
      IF(NT.EQ.1)GOTO 55
      TYPE 9
      FORMAT(/,3X,'CENTER  ',6X,'CURRENT POSITION',/)
      DO 20 I=1,IPTS
      TYPE 10, I,CENTER(1,I)
10      FORMAT(1X,'CENTER(',I3,') = ',F)
20      CONTINUE

C      INPUT ABSOLUTE LINE FOR CALIBRATION.
      TYPE 30
30      FORMAT(/,1X,'INPUT WHICH CENTER IS TO BE USED
      1 FOR ABSOLUTE FREQ. CALIBRATION?'$)
      ACCEPT *,IABS
      TYPE 35
35      FORMAT(/,1X,'WHAT IS ITS ABSOLUTE FREQUENCY ?'$)
      ACCEPT *,ABCAL
      NT=1
      RETURN
CHANGE CURRENT ARRAY TO RELATIVE FREQUENCY.
55      CONTINUE
      CALL RLFREQ(DAVE,IPTS)
      DIFF = ABCAL - CENTER(1,IABS)
CHANGE RELATIVE ARRAY TO ABSOLUTE FREQS
      DO 60 L=1,IMAX(3)
      ETCUR(L)=ETCUR(L)+DIFF
60      CONTINUE
C      DO 70 I=1,10
C      TYPE 75,I,ETCUR(I)
75      FORMAT(1X,'ETCUR(',I2,') = ',F)
70      CONTINUE
      RETURN
      END
C-----

```

```

SUBROUTINE TAU(P3,IPTS,K2,K3,K4)
  DIMENSION COF(501),CUR(501),EMPTY(501),GAS(501)
  DIMENSION CSI(3,2),ETCUR(501),IMAX(4)
  COMMON/A/CUR,EMPTY,GAS
  COMMON/B/CSI,ETCUR,IMAX
  DOUBLE PRECISION FILEA
C  PURPOSE:
C  TAU CALCULATES AN ARRAY OF ABSORPTION COEFFICIENTS
C  USING THE BEER-LAMBERT LAW:
TRANSMITTANCE=EXP(-COF)(XL)(P3)
C  THEN APPENDS THIS DATA TO A FILE (OPTIONAL).
C  MAJOR VARIABLES:
C  XL = CELL LENGTH (CM)
C  COF = ABSORPTION COEFFICIENT
C  EMPTY(K)/GAS(K) = TRANSMITTANCE
C  P3 = GAS PRESSURE IN CELL
C  IMAX(2) = OF DATA PTS IN GAS CURVE. (FROM CURFIT)
CELL LENGTH IS SET HERE
  XL= 50.0
CALCULATE ABSORPTION COEFFICIENTS.
  DO 10 K=1,IMAX(2)
    COF(K)=(-ALOG(GAS(K)))/(P3*XL))
  10  CONTINUE
  CALL EPLLOT(COF,IPTS,3)
C APPENDING ROUTINE.
  TYPE 61
61  FORMAT(1X,'DO YOU WANT ABS COFS APPENDED TO A DATA
FILE? '$)
  ACCEPT 62,ANS
62  FORMAT(A5)
  IF(ANS.EQ.'NO') GO TO 75
  TYPE 63
63  FORMAT(1X,'FILE NAME? '$)
  ACCEPT 622,FILEA
622  FORMAT(A10)
  OPEN(UNIT=21,ACCESS='APPEND',FILE=FILEA)
C
C  ONLY WRITE OUT MULTIPLES OF 5 DATA PAIRS
C
  ITES=IMAX(2)/5
  IT=5*ITES
C  TYPE *,IMAX(2),ITES,IT
  WRITE(21,*)IT,K2,K3,K4,P3
C  APPEND TRANSMITTANCES TO DATA FILE
C
  WRITE(21,999)((ETCUR(I),COF(I),I=J,J+4),J=1,IT,5)
999  FORMAT(5(1X,F,1X,F))
75  CONTINUE
  RETURN
  END
C

```


C-----

C

```

      SUBROUTINE READDT(X,Y,N)
      DIMENSION X(1),Y(1)
      READ(21,END=22,334) ( (X(I),Y(I),I=J,J+4),J=1,N,5)
334      FORMAT(10(F7.4,1X) )
      C      WRITE(5,*) ( (X(I),Y(I),I=J,J+4),J=1,N,5)
      RETURN
22      CONTINUE
      TYPE 33
33      FORMAT(' RAN OUT OF DATA IN READDT---RECAP
FOLLOWS')
      TYPE 34 ,N
34      FORMAT(' NUMBER OF DATA POINTS =' ,I)
      WRITE(5,*) ( (X(I),Y(I),I=J,J+4),J=1,N,5)
      RETURN
      END

```

C-----

```

      SUBROUTINE TRANS(P3,IPTS,K2,K3,K4)
      DIMENSION CUR(501),EMPTY(501),GAS(501),TRA(501)
      DIMENSION CSI(3,2),ETCUR(501),IMAX(4)
      COMMON/A/CUR,EMPTY,GAS
      COMMON/B/CSI,ETCUR,IMAX
      DOUBLE PRECISION FILEA

      C  PURPOSE:
      C  APPENDS TRANSMITTANCE DATA TO A FILE (OPTIONAL).
      C  MAJOR VARIABLES:
      C  TRANSMITTANCE (TRA) =GAS(K)/EMPTY(K) (CALCULATED IN
      C  NORMAL)
      C  IMAX(2) = OF DATA PTS IN GAS CURVE. (FROM CURFIT)
      C  TYPE *,IMAX
      C  DO 10 K=1,IMAX(2)
      C  TRA(K) = GAS(K)/EMPTY(K)
10      CONTINUE
      C APPENDING ROUTINE.
      TYPE 61
61      FORMAT(1X,' WANT TRANSMITTANCES APPENDED TO A DATA
FILE?'$)
      ACCEPT 62,ANS
62      FORMAT(A5)
      IF(ANS.EQ.'NO') GO TO 75
      TYPE 63
63      FORMAT(1X,'FILE NAME?'$)
      ACCEPT 622,FILEA
622      FORMAT(A10)
      OPEN(UNIT=21,ACCESS='APPEND',FILE=FILEA)

      C
      C  ONLY WRITE OUT MULTIPLES OF 5 DATA PAIRS
      C
      ITES=IMAX(2)/5

```

```
      IT=5*ITES
C      TYPE *,IMAX(2),ITES,IT
      WRITE(21,*)IT,K2,K3,K4,P3
C      APPEND TRANSMITTENCES TO DATA FILE
C
      WRITE(21,999)( (ETCUR(I),GAS(I),I=J,J+4),J=1,IT,5)
999      FORMAT(5(1X,F,1X,F))
75      CONTINUE
      RETURN
      END
```

APPENDIX B

PROGRAM VFIT

Program VFIT is listed in this appendix as discussed in the section Data Analysis. It is written to run in an interactive mode and uses plotting routines from the Tektronix PLOT10 graphics package and from Bevington [4]. The program is coded in Fortran-10 and is designed to run on a 36 bit DecSystem-10 time shared computer under the Tops10 monitor Version 6.03A. Some of the Format statements use the Fortran-10 free field characteristics (F instead of Fw.d) and a few DO loops have indicies that are non-integer. Otherwise, this code conforms to the ANSI standard.

```

PROGRAM VFIT
DIMENSION KV(500),V(500),KABS(500)
DIMENSION X(500),Y(500),SIGMAY(500),A(5)
DIMENSION YFIT(300)
DIMENSION ZVAL(300),ZIND(300)
DIMENSION RES(20),YGUESS(20)
REAL KV,KABS,LN2,MASS,KBOLTZ,K0,KMAX
REAL K1,K2,K3
DOUBLE PRECISION XFILE

```

```

C
C
C      THIS PROGRAM IS DESIGNED TO READ IN ABSORPTION
C      COEFFICIENT DATA FOR A SINGLE LINE AND FIT
C      A VOIGT FUNCTION TO IT.
C
C
C

```

```

C      VOIGT FUNCION IS GENERATED BY THE FUNCTIONS
C      K,K1,K2,K3 AS DESCRIBED BY B.H. ARMSTRONG
C      IN JQSRT 7,PP 61-88, (1967).
C
C
C

```

```

C      THESE ARE ASSEMBLED IN THE FILE ARM.FOR
C
C
C

```

```

C      WRITTEN BY DR. G.E. COPELAND AND L.N. MAJORANA
C      DEPT OF PHYSICS
C      OLD DOMINION UNIVERSITY
C      NORFOLK, VA 23508
C
C
C

```

```

C      DATA ARE IN FILE COF?.DAT
C

```

```

C      INPUT DATA LOOKS LIKE THIS
C 360, 12, 3, 79, 0.2600000
C NPTS, MON, NDAY, NYEAR, PRESSURE IN TORR
C 1129.3619 -0.0000081 1129.3623 -0.000016/ 1129.3626
-0.0000303 1129.3629 -0.0000414 1129.3632 -0.0000426
C      FREQUENCY IN CM-1 FOLLOWED BY ABS COEFFICIENT BASE
E
C      5 DATA PAIRS PER LINE
C
C      OPEN THE DATA FILE
      TYPE 82
82      FORMAT(' INPUT THE NAME OF THE DATA
FILE<COF?.DAT>?'$)
      ACCEPT 83,XFILE
83      FORMAT(A10)
      OPEN(UNIT=21,ACCESS='SEQIN',FILE=XFILE)
      READ(21,*)NPTS,MON,NDAY,NYEAR,PRES
      TYPE 381,PRES,XFILE
381      FORMAT(' PRESSURE =',F5.2,' TORR DATA FROM ',A10)
      DO 10 I=1,NPTS,5
      READ(21,*)(V(J),KABS(J),J=I,I+4)
10      CONTINUE
      CLOSE(UNIT=21)
      TYPE 71
71      FORMAT(' INPUT THE MODE FOR THE FILE?<1,0,-1>?'$)
      ACCEPT *,MODE
C
C
C      FIND THE CENTER OF THE SPECTRAL LINE
C
      YMAX=-10.
      DO 20 I=1,NPTS
      IF(KABS(I) .GT. YMAX)JJ=I
      IF(KABS(I) .GT. YMAX)YMAX=KABS(I)
20      CONTINUE
      TYPE 221,JJ,YMAX
221      FORMAT(' MAX OCCURS AT ',I3,' AND VALUE IS
',1PE)
C
C
C      REMOVE 1129 CM-1
      DO 22 I=1,NPTS
22      V(I)=V(I)-1129.
C
C      YMAX IS THE MAX OF THE ABS COEFFICIENT
C      JJ IS POINT IN DATA IT OCCURS
C
C      TYPE *,JJ,YMAX
C      GRAB ABOUT 10 POINTS AROUND JJ AND FIT A QUADRATIC
C      TO THE DATA BY CALLING POLFIT...
C      Y=A(1)+A(2)*X+A(3)*X*X

```

```

C      THEN THE POSITION OF THE MAX OF POLYNOMIAL
C      WILL BE THE CENTER LINE FOR ALL FUTURE CALCULATIONS
C
C      GENERATE THE X AND Y ARRAYS FOR FITTING
C
      NST=JJ-3
      NFIN=JJ+3
      NK=0
      DO 30 I=NST,NFIN
      NK=NK+1
      X(NK)=V(I)
30      Y(NK)=KABS(I)
C
C      TYPE *,X,Y
C      PAUSE
C
C      GENERATE THE MEAN AND ESTIMATED ERRORS FOR A SET OF
DATA      CALL XFIT(Y,SIGMAY,NK,MODE,YMEAN,SIGMAM,SIGMA
      DO 833 I=1,NK
833      SIGMAY(I)=SQRT(( Y(I)-YMEAN)**2/(FLOAT(NK)-1.))
C
C      BEVINGTON P76
C
C      NOW CALL POLFIT BEVINGTON P140
      CALL POLFIT(X,Y,SIGMAY,NK,3,MODE,A,CHISQR)
      DO 49 I=1,NK
      ZVAL(I)=A(1)+A(2)*X(I)+A(3)*X(I)**2
C      1+A(4)*X(I)**3!          +A(5)*X(I)**4
49      CONTINUE
C      TYPE *,X,Y,ZVAL
      PAUSE
      CALL PLOT(X,Y,NK,X,ZVAL,2,PRES,XFILE)
C      PAUSE
C      TYPE *,CHISQR,A
C
C      CENTER OF THE LINE IS AT -A(2)/(2.*A(3))
      VCEN=-A(2)/(2.*A(3))
C      FMAX=A(1)+A(2)*VCEN+A(3)*VCEN**2
      TYPE 33,VCEN
33      FORMAT(' CENTER FREQUENCY =',F)
C
C      STRIP OUT THE LINE CENTERS
      DO 50 I=1,NPTS
50      V(I)=V(I)-VCEN
C
CALCULATE THE DOPPLER WIDTH
      PI=3.141592654
      SQPI=SQRT(PI)
C
      MASS=3.*15.9994

```

```

C      C=2.99/9250E10
C      SPEED OF LIGHT IN CM/S
C      KBOLTZ = 1.380622E-16
C      BOLTZMAN CONSTANT ERG/K
C      T=285.
C      TEMP IN KELVIN
C      AMU=1.660531E-24
C      1AMU IN GRAMS
C      LN2=ALOG(2.)
C      SRLN2=SQRT(LN2)

C      AD=SQRT( 2.*KBOLTZ*T*LN2/(MASS*AMU))/C
C      AD=AD*(1129.+VCEN)
C      AD1=AD*1000.
C      AD2=AD1*C/1.E+9
CTYPE *,AD2
C      TYPE 331,AD1,AD2
331      FORMAT(' DOPPLER WIDTH<FWHM> ='1PE'
MILLIKAYSEERS'OPF8.3'MHZ')
C
C      CALCULATE THE 1ST APPROXIMATION TO THE LINE STRENGTH S
C
C      NEED TO GET A DIFFERENT PIECE THAN WE DID FOR THE
LINE CENTER
C      DETERMINATION.....THE NARROWER THE LINE THE LESS
WE NEED
C      THE WIDER THE LINE THE MORE WE NEED.
C      THIS IS DETERMINED BY PRESSURE
C      WE COULD LOOK AT THE PRESSURE BUT INSTEAD LETS
C      COUNT THE NUMBER OF POINTS ABOVE
C      THE 10% LEVEL OF THE PEAK
C      IF THIS IS GREATER THAN 12 WE WILL GET
C      ONLY +/- 25 POINTS
C
C      REPORT THE CUTOFF CRITERIAN-----CUTOFF VALUE
C
C
C      IF THIS IS LARGER WE WILL GET MORE POINTS FOR A
BETTER
C      WING FIT
C      CUTOFF=0.1*YMAX
C      TYPE 44 ,CUTOFF
44      FORMAT(' CUTOFF IS 10 PERCENT OF YMAX ',F)
C      ICUT=0
C      DO 469 I=1,NPTS
C      IF( KABS(I).GT.CUTOFF) ICUT=ICUT+1
469      CONTINUE
C      TYPE *,ICUT
C      PAUSE
C      IEXTRA=30

```

```

IF( ICUT.GE. 16) IEXTRA=40
NST=JJ-IEXTRA
NFIN=JJ+IEXTRA
NK=0
DO 303 I=NST,NFIN
NK=NK+1
X(NK)=V(I)
303   Y(NK)=KABS(I)
C
C
C   S=AREA(X,Y,NK,3)
C   TYPE *,S
C
C   GENERATE KO
C
C   KO=(S/AD)*SRLN2/SQPI
C   TYPE 990,KO
990   FORMAT(' DIMENSIONAL CONSTANT OF THE REDUCED
ABSORPTION
      1 COEFFICIENT =',1PE)
C
C   GENERATE THE VARIABLE X
C
C   CUT OFF POINTS ON FAR WINGS
C   JL=JJ-IEXTRA
C   JR=JJ+IEXTRA
C   NP=0
C   DO 88 I=JL,JR
C   NP=NP+1
88   X(NP)=V(I)*SRLN2/AD
C   TYPE *,V
C
C   TYPE 451,NP
451   FORMAT(' TOTAL NUMBER OF DATA PAIRS USED IN
ANALYSIS =',I4)
C
C   GENERATE THE KABS DATA IN NORMAL FORM KABS/KO
C   NP=0
C   DO 89 I=JL,JR
C   NP=NP+1
89   KV(NP)=KABS(I)/KO
C
CALL A PLOTTING ROUTINE
C   CALL PLOT(X,KV,NP,X,KV,0,PRES,XFILE)
C
C
C   GUESS WHAT THE INTIAL VALUE OF Y =AL*SQLN2/AN IS???
C
C   USE THE FUNCTIONS K(X,Y) WITH X=0.0 TO GUESS THE
START UP OF Y

```

```

C
C      KMAX= VALUE OF THE K FUN
      KMAX=-10.
      DO 41 I=1,NP
      IF(KMAX .LT. KV(I) ) KMAX = KV(I)
41      CONTINUE
      TYPE 991,KMAX
991      FORMAT(' MAX VALUE OF KABS/K0(AT LINE CENTER)
      =',F)
      NZ=0
      DO 66 Z=0.0,3.0,0.025
      NZ=NZ+1
      ZIND(NZ)=Z
66      ZVAL(NZ)=ARM(0.0,Z)
C      TYPE *,ZVAL
C
CALL A ROUTINE TO INTERPOLATE TO GET CLOSER TO THE REAL Y
VALUE
C
      CALL INTERP(ZVAL,ZIND,NZ,3,KMAX,YOUT)
      TYPE 992,YOUT
992      FORMAT(' INTERPOLATED VALUE OF Y =',F)
      DO 661 I=1,NP
661      ZVAL(I)=ARM(ABS(X(I)),YOUT)
C      TYPE *,ZVAL
      PAUSE
      CALL PLOT(X,KV,NP,X,ZVAL,2,PRES,XFILE)
C
C      NOW WE HAVE A GOOD GUESS FOR THE VOIGT PROFILE
C
C      WILL CHANGE THE Y VALUE OVER 10 VALUES OR SO AND
CALCULATE
C      THE CHI SQUARE TO THE DATA AND FIND MINIMUM Y FOR
THOSE AND REDO
C      UNTIL CHI SQUARE IS MINIMUM
C
C      X ARRAY HAS THE INDEPENDENT VARIABLES IN REDUCED
FORM.
C      KV ARRAY IS THE REDUCED DATA
C      ZVAL IS THE FITTED DATA
C      NP IS NUMBER OF DATA POINTS
C
C      1ST START UP THE CHI SQR CALCULATION USING YOUT AS
THE
C      1ST VALUE OF THE K(X,Y)---THEORY FIT ABOVE
      DO 551 I=1,NP
551      SIGMAY(I)=0.0
      CALL XFIT(KV,SIGMAY,NP,MODE,YMEAN,SIGMAM,SIGMA)
C
CALCULATE THE SIGMAY'S
C

```



```

DO 561 I=1,NP
561   SIGMAY(I)=SQRT( ( KV(I)-YMEAN)**2/(FLOAT(NP)-1.)
)
NFREE=NP-2
REST=FCHISQ(KV,SIGMAY,NP,NFREE,MODE,ZVAL)
C
C   REST IS THE REDUCED CHI SQUARE FOR THE GUESS
YST=YOUT-YOUT/10.
YEND=YOUT+YOUT/10.
YSTEP=YOUT/100.
95   I=0
DO 552 YS=YST,YEND,YSTEP
I=I+1
552   YGUESS(I)=YS
ITOTAL =I
I=0
C
CALL THE FCHISQ ROUTINE
TYPE 441,I,REST,YOUT
DO 553 I=1,ITOTAL
C
CALCULATE THE ZVAL'S FOR THIS YGUESS
DO 554 J=1,NP
554   ZVAL(J)=ARM( ABS(X(J)) ,YGUESS(I) )
C
C   GENERATE THE SIGMAY'S
DO 5551 IK=1,NP
5551   SIGMAY(IK)=0.0
DO 5661 IH=1,NP
5661   SIGMAY(IH)=SQRT( (
KV(IH)-YMEAN)**2/(FLOAT(NP)-1.) )
CALL XFIT(KV,SIGMAY,NP,MODE,YMEAN,SIGMAM,SIGMA)
RES(I)=FCHISQ(KV,SIGMAY,NP,NFREE,MODE,ZVAL)
TYPE 441,I,RES(I),YGUESS(I)
441   FORMAT(' TRY ',I2,' REDUCED CHISR='1PE'Y ='1PE)
C
C
C   SKIP OUT IF REDUCED CHISQ DOES NOT CHANGE BY 0.C05
C   IF( I.EQ.1) GOTO 553
C
C   IF(ABS( ( RES(I)-RES(I-1) )/RES(I) ) .LT. 0.005)
IKEEP=I
C   IF(ABS( ( RES(I)-RES(I-1) )/RES(I) ) .LT. 0.01)
GOTO 6812
553   CONTINUE
68   CONTINUE
YMIN=10.
DO 69 I=1,ITOTAL
IF( RES(I) .LT. YMIN) IKEEP=I
IF( RES(I) .LT. YMIN) YMIN=RES(I)

```

```

69      CONTINUE
      IF( IKEEP.EQ. ITOTAL) TYPE 510
510     FORMAT(' OOPS!  STILL DECREASING AT EDGE OF
SEARCH. I WILL
      1CONTINUE....')
      IF( IKEEP.EQ. ITOTAL) YST=YEND
      IF( IKEEP.EQ. ITOTAL) YEND=YST+YOUT/10.
      IF( IKEEP.EQ. ITOTAL)GOTO 95
6812    TYPE 690,YGUESS(IKEEP)
690     FORMAT(' RATIO OF LORENTZ TO DOPPLER WIDTH
=' ,1PE)
      AL=YGUESS(IKEEP)*AD/SRLN2
      AL1=AL*1000.
      AL2=AL1*C/1.E+9
      TYPE 691,AL1,AL2
691     FORMAT(' LORENTZ WIDTH ',1PE,' MILLIKAYERS
='OPF8.3,' MHZ')

C      PAUSE
C
C PREPARE A RICHER ARRAY FOR PLOTTING MAKE IT 3*NP LONG
C
C      1ST DO THE X ARRAY
C      PUT NEW X ARRAY IN V
C      PUT DATA Y ARRAY IN KABS
C      PUT NEW FITTED DATA IN Y
      NF3=3*NP
      DO 46 I=1,NPTS
46      KABS(I)=0.0
      DO 461 I=1,NPTS
461     V(I)=0.0
      IL=1
      DO 4 J=1,NP
      V(IL)=X(J)
      V(IL+1)=X(J)
      V(IL+2)=X(J)
      KABS(IL)=KV(J)
      KABS(IL+1)=KV(J)
      KABS(IL+2)=KV(J)
      IL=IL+3
47      CONTINUE
C      TYPE *,V,KABS
C
C CALCULATE A RICH NEW X ARRY FOR INDEPENDENT VARIABLE
C      FOR THE SECOND GRAPH OF FITTED VS. X
C
      XMIN=V(1)
      XMAX=V(NP3)

C
C      STOE NEW INDEPENT VARIABLE IN Y
C

```

```

XINC=2.*XMAX/FLOAT(NP3)
IC=0
DO 201 XO=XMIN,XMAX,XINC
IC=IC+1
201 Y(IC)=XO
C TYPE *,IC,NP3
C PAUSE
C
CALL ROUTINE TO GET THE NEW DEPENDENT VARIABLE AT THE SPACING
C DESIRED....XINC
C
C STORE IN ZVAL
DO 345 I=1,NP3
345 ZIND(I)=ARM( ABS(Y(I)),YGUESS(IKEEP))
C
PAUSE
CALL PLOT(V,KABS,NP3,Y,ZIND,2,PRES,XFILE)
END
C
C-----
C
SUBROUTINE PLOT(X,Y,NP,X1,Y1,IPLT,P,XFILE)
DIMENSION X(1),Y(1)
DIMENSION X1(1),Y1(1)
DIMENSION YLABEL(18),IYLAB(18)
DIMENSION TR(4)
DIMENSION XLABEL(48),IXLAB(48)
DIMENSION TITLE(22),ITIT(22)
DIMENSION TITLE2(28),ITIT2(28)
DOUBLE PRECISION XFILE
C
C DATA FOR THE TITLES FOR THE GRAPHS
C
DATA TITLE/'V','O','I','T','
','F','U','N','C','T','I','O','N'
1,'F','I','T',' ','F','O','R',' '/
C22 CHARACTERS
DATA TR/'T','O','R','R'/
C 4 CHARACTERS
DATA
XLABEL/'W','A','V','E','N','U','M','B','E','R',' ',
' 'S','C','A','L','E','['','D','O','P','P','L','E','R',' ',
' '
2'W','I','D','T','H','='','0','.','9','8','5','M','K','='','2',
3'9','.','5','M','H','Z','1'/
C48 CHARACTERS
DATA YLABEL/'R','E','D','U','C','E','D','
','A','B','S',' '
1'C','O','E','F','F','.'/
C18 CHARACTERS

```

```

DATA TITLE2/'O','3',' ','L','I','N','E',' ','
','A','T',' ','1','1'
','2','9',' ','4','4','3','C','M','-','1'
','F','R','O','M',' '/

```

C28 CHARACTERS

```

CALL INITT(240)
CALL BINITT
CALL NPTS(NP)
CALL XFRM(2)
CALL YFRM(2)
IF(IPLT .NE.0) CALL SYMBL(1)
IF(IPLT .NE.0) CALL LINE(-1)
CALL CHECK(X,Y)
CALL DISPLAY(X,Y)
IF(IPLT .EQ.2) CALL SYMBL(0)
IF(IPLT .EQ.2) CALL LINE(0)
IF(IPLT.EQ.2) CALL CPLOT(X1,Y1)
MOVE AND PUT ON LABELS

```

C
C

```

CALL MOVABS(20,600)
CALL KA12AS(18,YLABEL,IYLAB)
CALL VLABEL(18,IYLAB)
CALL KA12AS(48,XLABEL,IXLAB)
CALL NOTATE(325,20,48,IXLAB)

```

775

```

CONTINUE
CALL KA12AS(28,TITLE2,ITIT2)
CALL MOVABS(200,750)
CALL HLABEL(28,ITIT2)
CALL ANMODE
TYPE 10,XFILE

```

10

```

FORMAT(1X,A10)
CALL KA12AS(22,TITLE,ITIT)
CALL MOVABS(200,725)
CALL HLABEL(22,ITIT)
CALL ANMODE
TYPE 11,P

```

11

```

FORMAT(1X,F8.2)
CALL BELL
CALL TINPUT(IEND)
CALL ERASE
RETURN
END

```

C

C

CODE TO CALCULATE THE VOIGT PROFILE

C

C

C

C

C

C

```

TAKEN FROM
SPECTRUM LINE PROFILES:THE VOIGT FUNCTION
BY B.H. ARMSTRONG
JQSRT 7,PP61-88,(1967)

```

```

      FUNCTION ARM(X,Y)
C      THIS FUNCTION IS THE REAL PART OF THE COMPLEX
PROBILITY FUNCTION
C      OR THE VOIGT SPECTRUM LINE PROFILE
      REAL K1,K2,K3
      COMMON W(10),T(10),Y2
      DATA W/4.62243670E-1,2.86675505E-1,1.09017206E-1,
1      2.48105209E-2,3.24377334E-3,2.28338636E-4,
2
7.80255648E-6,1.08606937E-7,4.39934099E-10,2.22939365E-13/
      DATA
T/0.245340708,0.737473729,1.23407622,1.73853771,2.25497400,
1
2./3880606,3.34785457,3.94476404,4.60368245,5.38748089/
      Y2=Y*Y
C
C      TESTS
C
      IF(Y.LT.1.0.AND.X.LT.4.0.OR.Y.LT.1.8/(X+1.0)) GOTO
300
      IF(Y.LT.2.5.AND.X.LT.4.0) GOTO 200
100      ARM=K3(X,Y)
      RETURN
200      ARM=K2(X,Y)
      RETURN
300      ARM=K1(X,Y)
      RETURN
      END

```

C-----

```

C
      FUNCTION K1(X,Y)
      REAL K1
      DOUBLE PRECISION C(34),COEF,BN01,BN02,BN,X1,F
      F3(T)=EXP(T**2-X**2)
C      FROM HERE TO STATEMENT 30 WE CALCULATE DAWSON'S
FUNCTION
C      ENTER HUMMERS CHEBYSHEV COEFFICIENTS C(I)
      DATA C/ .199999999972224,-.184000000029998,
1
.1558399999965025,-.1216640000043988,.0877081599940391,
2
-.0585141248086907,.0362157301623914,-.0208497654398036,
3
.0111960116346270,-.56231896167109D-2,.26487634172265D-2,
4
-.11732670757704D-2,.48995199/8088D-3,-.1933630801528D-3,
5
.72287/446788D-4,-.256555124979D-4,.86620/36841D-5,
6 -.27876379719D-5,.8566873627D-6,-.2518433784D-6,

```

```

      7
.709360221D-/, -.191732257D-7, .49801256D-8, -.1244/734D-8,
      8
.299/7//D-9, -.696450D-10, .156262D-10, -.3389/D-11, .7116D-12,
      9 -.1447D-12, .285D-13, -.55D-14, .10D-14, -.2D-15/
      Y2=Y*Y
      IF((X**2-Y2).GT.70.0)GO TO 2
      U1=EXP(-X**2+Y2)*COS(2.*X*Y)
      GO TO 5
2      U1=0.0
5      IF(X.GT.5.0) GO TO 1000
C      CLENSHAW'S ALGORITHM AS GIVEN BY HUMMER
      BN01=0.0D0
      BN02=0.0D0
      X1=X/5.0D0
      COEF=4.0D0*X1**2-2.0D0
      DO 20 I=1,34
      II=35-I
      BN=COEF*BN01-BN02+C(II)
      BN02=BN01
20     BN01=BN
30     F=X1*(BN-BN02)
40     DN01=1.0-2.0*X*SNGL(F)
1100    DN02=SNGL(F)
      GO TO 1200
1000
DN01=-(.5/X**2+.75/X**4+1.875/X**6+6.5625/X**8+29.53125/X**10
+
      1 162.4218/X**12+1055.7421/X**14)
      DN02=(1.-DN01)/(2.*X)
1200    FUNCT=Y*DN01
      IF(Y.LE.1.0E-8) GO TO 2500
      Q=1.0
      YN=Y
      DO 2000 I=2,50
      DN=(X*DN01+DN02)*(-2.)/FLOAT(I)
      DN02=DN01
      DN01=DN
      IF (MOD(I,2))2000,2000,1500
1500    Q=-Q
      YN=YN*Y2
      G=DN*YN
      FUNCT=FUNCT+Q*G
      IF (ABS(G/FUNCT).LE.1.00E-08)GO TO 2500
2000    CONTINUE
2500    K1=U1-1.12837917*FUNCT
      RETURN
      END
C
C -----
C

```

```

      FUNCTION K2(X,Y)
      REAL K2
      COMMON W(10),T(10),Y2
      G=0.0
      DO 100 I=1,10
      R=T(I)-X
      S=T(I)+X
100   G=G+(4.*T(I)**2-2.)*(R*ATAN(R/Y)+S*ATAN(S/Y)-.5*Y*(ALOG(Y2+R*
      *2)
      1 +ALOG(Y2+S**2)))*W(I)
      K2=0.318309886*G
      RETURN
      END

```

C

C-----

C

```

      FUNCTION K3(X,Y)
      REAL K3
      COMMON W(10),T(10),Y2
      G=0.0
      DO 100 I=1,10
100   G=G+(1.0E0/((X-T(I))**2+Y2)+1.0E0/((X+T(I))**2+Y2))*W(I)
      K3=0.318309886*Y*G
      RETURN
      END

```